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Hydrogeochemistry of Saline Waters in Aquifers of Tertiary and Younger Age in Northeastern Louisiana and Southeastern Arkansas.

Glenn Fredrick Huff
Louisiana State University and Agricultural & Mechanical College

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Huff, Glenn Fredrick, Ph.D.

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300 N. Zeeb Rd.
Ann Arbor, MI 48106

HYDROGEOCHEMISTRY OF SALINE WATERS IN AQUIFERS OF TERTIARY AND YOUNGER AGE IN NORTHEASTERN LOUISIANA AND SOUTHEASTERN ARKANSAS

A Dissertation

Submitted to the Graduate Faculty of the
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by
Glenn F. Huff
B.S., West Georgia College, 1980
M.S., Georgia Institute of Technology, 1984
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I would never have started the Ph.D. program without the encouragement of my wife, Marilyn. She told me "you can do it" and I started to believe that I really could. Completion of this work required lots of time stolen from my wife and daughter, Selene. Dad plans to do better in the future.

This work is dedicated to my late parents Glenn T. and Regene P. Huff. They demonstrated to me respect for knowledge and a desire to do the job right. Along with lots of love, these are debts which can never be repaid.

Much of the data used in this work was provided by the U.S. Geological Survey. All interpretations of data in this work are solely those of the author and are not endorsed by the U.S. Geological Survey.

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ABSTRACT

Solute source tracing using Br/Cl and $^{87}Sr/^{86}Sr$ ratios indicate that the source of brackish water in the Mississippi River alluvial and Jasper aquifers of Concordia Parish, Louisiana are brines and saline waters from the Wilcox aquifer. The proximity of maximum concentrations of dissolved solids to the location of plugged and abandoned oil wells and test holes indicates that brines and saline waters have migrated upward through these oil wells and test holes.

Br/Cl ratios in the Wilcox aquifer suggest dissolution of halite as a major source of dissolved solids. Apparent thermodynamic equilibrium exists between plagioclase and kaolinite, plagioclase and Na-smectite, microcline and albite, and illite and Ca-smectite. The presence of a $(Ca,Mg,Sr)CO_3$ solid solution may buffer concentrations of dissolved Mg and Sr. Values of $\delta^{18}O$ may also be buffered by water-rock interaction.

Values of $^{87}Sr/^{86}Sr$ in conjunction with regional ground-water flow indicates that solutes in the upper unit of the Wilcox aquifer were derived from the North Louisiana Salt Dome Basin while solutes in the middle unit were derived from the Gulf Coast Salt Dome Basin. If so, solutes in both the upper and middle units have been transported over considerable lateral distances by ground-water flow to reach their current locations.

The majority of brackish water in the Mississippi River alluvial aquifer in southeastern Arkansas is derived from saline waters in underlying Tertiary aquifers. Br/Cl ratios of brackish water indicate that a small part (approximately 5%) of the solutes within an area of anomalous salinity may be derived from brines of the Smackover Formation. The presence of the area of anomalous salinity in conjunction with the intersection of regional wrench faults also supports the idea that upward flow may be channeled through the area of intersection of these faults.

Once present in the alluvial aquifer of southeastern Arkansas, brackish water flows to the southwest along a fluvial channel at the base of the alluvial deposits. Estimated flow velocities indicate that significant southwestward movement of brackish water could occur on a human time scale.

CHAPTER I

INTRODUCTION

PURPOSE

Ground waters having elevated salinities are found in geohydrologic settings of widely varying geologic age and lithologic character. Environmental deterioration occurs if these waters having elevated salinities migrate into otherwise fresh water aquifers. Knowledge of potential sources and migration pathways of saline waters into fresh water aquifers can therefore be of great importance to planners and water resource managers. In contrast to the environmental problems they may cause, saline subsurface waters can provide information on processes controlling the migration and entrapment of hydrocarbons and the deposition of ore bodies.

Both the problems and the potential benefits of saline subsurface waters are found in the Louisiana Gulf Coast. The presence of brackish water in the Mississippi River Alluvial Aquifer is a recognized environmental problem both locally (Sanford, 1973; Fitzpatrick, 1985) and regionally (Hosman and others, 1968; Whitfield, 1975) in northern Louisiana and southern Arkansas. Conversely, the work of Carpenter and others (1974) and of Kharaka and others (1987) indicate that

subsurface saline waters may have been instrumental in emplacement of Mississippi Valley type ore deposits.

Obviously, understanding the migration pathways and geochemistry of subsurface saline waters is potentially both environmentally and economically important. To that end, this dissertation will discuss the origins and locations of brackish water in two study areas in the Mississippi River Alluvial Aquifer of Louisiana and extreme southern Arkansas. The occurrence of brackish water in this dominantly freshwater aquifer will be explained both in terms of natural hydrologic and anthropogenic processes. The hydrogeochemistry of oilfield brines in the Wilcox aquifer of eastern central Louisiana also will be discussed. Finally, data presented here in conjunction with data from the published literature will be synthesized to give an enhanced understanding of regional ground water flow and saline water geochemistry in the Louisiana Gulf Coast.

TERMINOLOGY

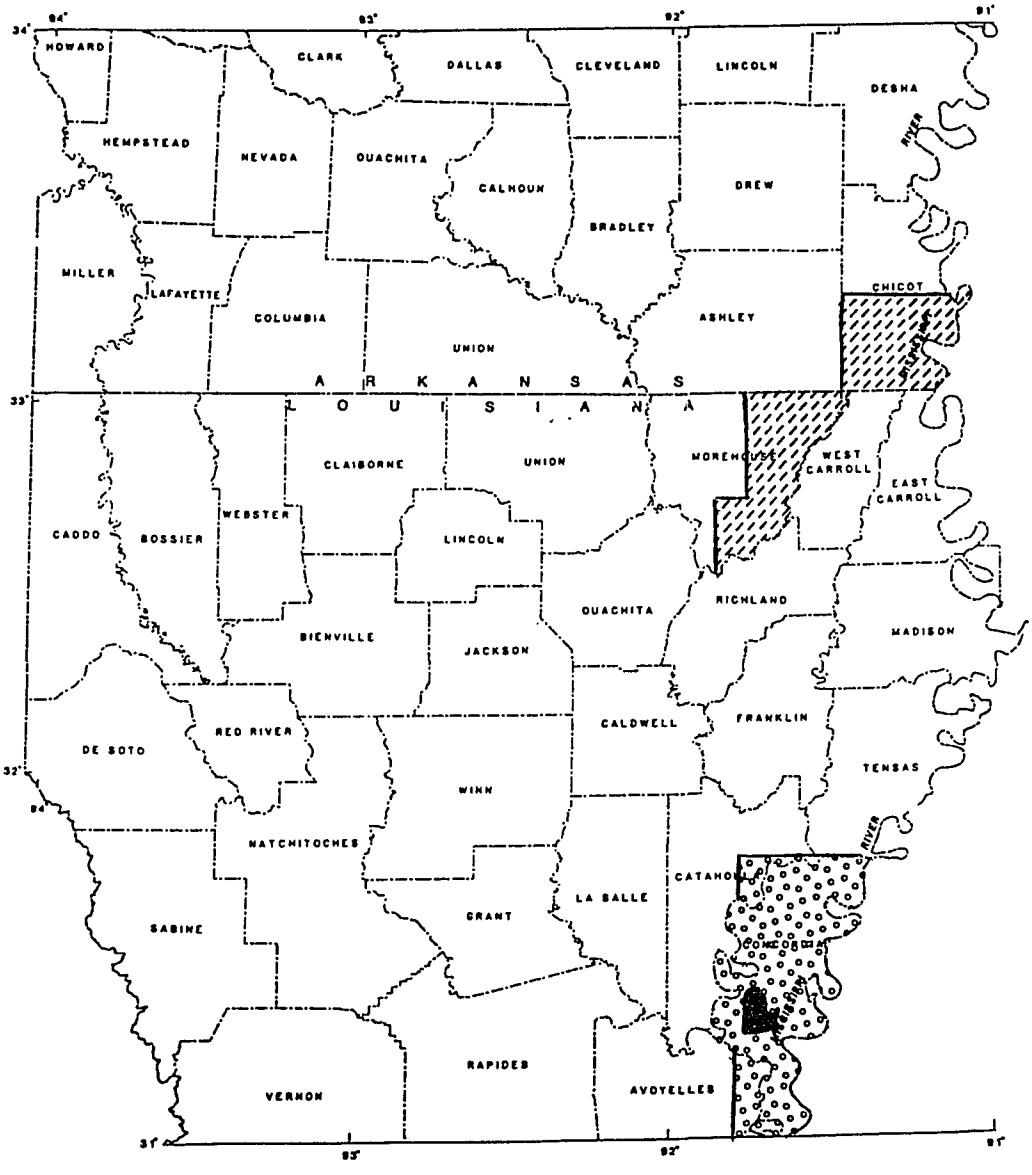
Henceforth, the terminology used in classifying subsurface waters based on concentrations of dissolved solids will be that of Carpenter (1978): fresh water, dissolved solids $< 1{,}000$ mg/L; brackish water, $1{,}000$ mg/L $\leq$ dissolved solids $< 10{,}000$ mg/L; saline water, $10{,}000$ mg/L $\leq$ dissolved solids $< 100{,}000$ mg/L; and brine, dissolved solids $\geq 100{,}000$ mg/L. The term confining unit will be used to

indicate a shale or clay layer of relatively low bulk hydraulic conductivity which forms the upper or lower boundary of an aquifer. An aquifer is defined as a unit having relatively high hydraulic conductivity which will produce a usable amount of water to a pumping well under normal conditions. To conserve space and enhance readability the Mississippi River Alluvial Aquifer will be referred to as the Alluvial Aquifer throughout this dissertation. Because of the hydrogeologic emphasis of this dissertation, hydrogeologic nomenclature will be emphasized throughout. All values of hydrogen and oxygen isotopic data are reported relative to standard mean ocean water (SMOW).

LOCATION AND SELECTION OF STUDY AREAS

Concordia Parish Study Area

The Concordia Parish study area includes Concordia and immediately adjacent areas of Avoyelles and Catahoula Parishes (fig 1.1). Water from the Alluvial Aquifer was extensively used for agricultural irrigation in the subset of the Concordia Parish study area (fig. 1.1) from 1976 through 1982. In 1982 salinity of irrigation water began to cause damage to irrigated crops (Lee Bean, Angelina Plantation Farms, personal communication, 1988). A history of oil exploration and production from the Wilcox aquifer in the Concordia Parish study area led to speculation that



CONCORDIA PARISH STUDY AREA

SUBSET OF CONCORDIA PARISH STUDY AREA CONTAINING SAMPLED IRRIGATION AND MONITOR WELLS

MOREHOUSE PARISH STUDY AREA

Figure 1.1 Concordia and Morehouse Parish study areas plus the subset of the Concordia Parish study area containing sampled irrigation and monitor wells.

salinity in the Alluvial Aquifer may have resulted from leakage of plugged and abandoned oil wells (Pat McHenry, Louisiana Department of Transportation and Development, personal communication, 1988). Study of Louisiana Department of Natural Resources log files showed the presence of at least 16 plugged and abandoned oil wells and test holes in the subset of the Concordia Parish study area.

Samples of brine and saline ground water were collected from producing oil wells screened in the Wilcox aquifer. Samples of fresh and brackish ground water were collected from irrigation and monitor wells screened in the Alluvial Aquifer and from the underlying Jasper aquifer system in the subset of the Concordia Parish study area shown in figure 1.1.

The presence of brackish water within the Alluvial Aquifer and the uppermost part of the immediately underlying Jasper aquifer system provided the opportunity to test the hypothesis that brackish water originated from the Wilcox aquifer. The investigative strategy was to use geochemical signatures of Br, Cl, and Sr in water from irrigation, monitor, and oil wells to establish the source of brackish water in the Alluvial Aquifer and uppermost part of the Jasper aquifer system (Chapter II). A discussion of the applications and limitations of geochemical signatures as tracers of origins of subsurface waters can be found in Appendix I.

In addition to providing needed data in Chapter II, sampling and analysis of brines and saline waters from the Wilcox aquifer in the Concordia Parish study area adds to knowledge of the origins of oil-field brines in eastern central Louisiana (Chapter III). The investigative strategy was to interpret the geochemistry (in particular the isotopes of O, H, and Sr and the systematics of Br and Cl) of saline waters and brines in the Wilcox aquifer in the context of regional ground water flow. In addition, the subsurface distributions of salinity, density, and viscosity of ground water in the Wilcox aquifer was determined using data from SP logs. These distributions could shed further light on hydrogeologic processes occurring in the Wilcox aquifer of eastern central Louisiana. Calculation of salinity, density, and viscosity of ground waters using SP logs can be found in Appendix II. The effects of mineral equilibria on the composition of Wilcox brines and saline waters was evaluated using selected thermodynamic data and speciation models. A discussion of speciation models used and how mineral equilibria calculations are made can be found in Appendix III. Current and historical work on the hydrogeology and geochemistry of waters in the Wilcox aquifer are discussed in a following section.

Morehouse Parish Study Area

The Morehouse Parish study area includes the eastern one third and portions of south central Morehouse Parish, Louisiana and an adjoining part of southern Chicot County, Arkansas (fig 1.1). This study area will be collectively referred to as the Morehouse Parish study area. In 1988, drought conditions were associated with an unprecedented number of rice crop failures and unprecedented use of ground water from the Alluvial Aquifer for crop irrigation in Morehouse Parish, Louisiana. These crop failures were mostly confined to a relatively narrow band in the northern third of Morehouse Parish from the Morehouse - West Carroll Parish line westward for up to approximately 16 km (10 mi). Salinity of ground water used for irrigation was suspected as a cause in crop failures (J.C. Stevens, Louisiana Agricultural Extension Service, personal communication, 1988).

Brackish water in the Alluvial Aquifer had been reported to occur on a local scale in northeastern Morehouse Parish by Sanford (1973). However, the areal extent of rice crop failures in 1988 was considerably larger than the known area of brackish water. This suggested that the area of brackish water in the Alluvial Aquifer of northeastern Morehouse Parish may have grown measurably over a period of only 15 to 20 years. In addition to possible growth, the

source(s) and hydrogeologic controls on the areal distribution of brackish water were unknown.

A band of ground water having elevated salinities (based on Cl concentrations of 100 to 250 mg/L) had been mapped in northern Louisiana including adjoining West Carroll Parish by Whitfield (1975). The extension of this band into Arkansas was documented by Boswell and others (1968). In addition, an area of brackish water within this band of elevated salinities had been mapped near the Morehouse Parish, Louisiana - Chicot County, Arkansas state line by Boswell and others (1968) and in more detail by Fitzpatrick (1985). The relationship between the areas mapped by Boswell and others (1968), Whitfield (1975), and Fitzpatrick (1985) and the proposed area of brackish water in the Alluvial Aquifer of Morehouse Parish were unknown. Further, the exact origins and hydrogeologic processes giving rise to the areas of elevated salinities mapped by Boswell and others (1968), Whitfield (1975), and Fitzpatrick (1985)) were also unknown.

The investigative strategy included the use of Br-Cl systematics and bulk chemical data to determine the possible source(s) of brackish water in the Alluvial Aquifer of Morehouse Parish and Chicot County. The roles of paleotopography, faulting, and regional ground water flow patterns on the distribution and possible sources of brackish water in the Alluvial Aquifer of northern Louisiana

and extreme southern Arkansas were also considered (Chapter IV).

Current and historical work on the hydrogeology and geochemistry of waters in the Alluvial Aquifer of northern Louisiana and southern Arkansas are discussed in a following section. Samples of fresh and brackish ground water were collected from irrigation and monitor wells screened in the Alluvial Aquifer of both Morehouse Parish, Louisiana and southern Chicot County, Arkansas and from the underlying Cockfield aquifer in Morehouse Parish.

WATER SAMPLE COLLECTION AND ANALYSIS

Irrigation, observation, and monitor wells were pumped until field measurements of pH, temperature, and specific conductance of the produced water reached stable values. Values of pH, temperature, specific conductance, and alkalinity were determined on unfiltered samples. Alkalinity was determined by titration to an end point of pH 4.5 with nitric acid immediately following sample collection. Water samples for cation and anion analysis were passed through a 0.45 μm filter and collected in pre-rinsed polyethylene bottles. Water samples for cation analysis were preserved by acidification to a pH of approximately 1.5 using nitric acid (Wood, 1976).

Samples of brine and saline ground water were collected from producing oil wells in the Concordia Parish study area

using methods described by Lico and others (1982). Only oil wells which had not been subjected to secondary recovery procedures such as steam or water injection or injection of surfactant chemicals were chosen for sampling. Any addition of chemical agents added to the production stream at the wellhead was discontinued for at least 15 minutes prior to taking a sample.

Wells sampled typically produced a mixture of oil, natural gas, and brine or saline water. Samples of this mixture were collected from valves near the wellhead into polyethylene carboys with spigots at the base and allowed to gravitationally separate. Water samples were than taken from the carboy spigot and passed through glass wool to further separate oil and brine or saline water. Samples for determination of specific conductance, alkalinity, $^{87}Sr/^{86}Sr$ ratios, $\delta^{18}O$, and δD were collected following filtration through glass wool.

Specific conductance and alkalinity were determined in the field. Because organic acid anions can contribute significantly to the alkalinity of oilfield ground waters (Willey and others, 1975), alkalinity of brine and saline water samples were determined by incremental titration with nitric acid. Incremental titrations were carried to at least a pH of 3.5 to ensure titration of all organic species which could have contributed to alkalinity. Following filtration through glass wool, brine or highly saline water samples for analysis of cations and anions were filtered, preserved, and

analyzed in the same manner as were samples from irrigation, observation, and domestic wells.

All quantitative elemental analyses not done in the field were carried out by the U.S. Geological Survey (USGS) National Water Quality Laboratory in Arvada, Colorado. Analytical precision of all measurements carried out by USGS National Water Quality Laboratory are given by Fishman and Friedman (1985). Analyses of all water samples for values of $^{87}Sr/^{86}Sr$ were carried out by Geochron Laboratories in Cambridge, Massachusetts. Analytical precision of $^{87}Sr/^{86}Sr$ measurements carried out by by Geochron Laboratories were $\pm$ 0.00002. Analysis of all water samples for values of $\delta^{18}O$ and δD were carried out by the USGS Isotope Fractionation Laboratory in Reston, Virginia. Analytical precision of $\delta^{18}O$ and δD measurements were $\pm$ 0.15 o/oo and $\pm$ 2 o/oo respectively.

HYDROGEOLOGIC OVERVIEW OF THE GULF COAST

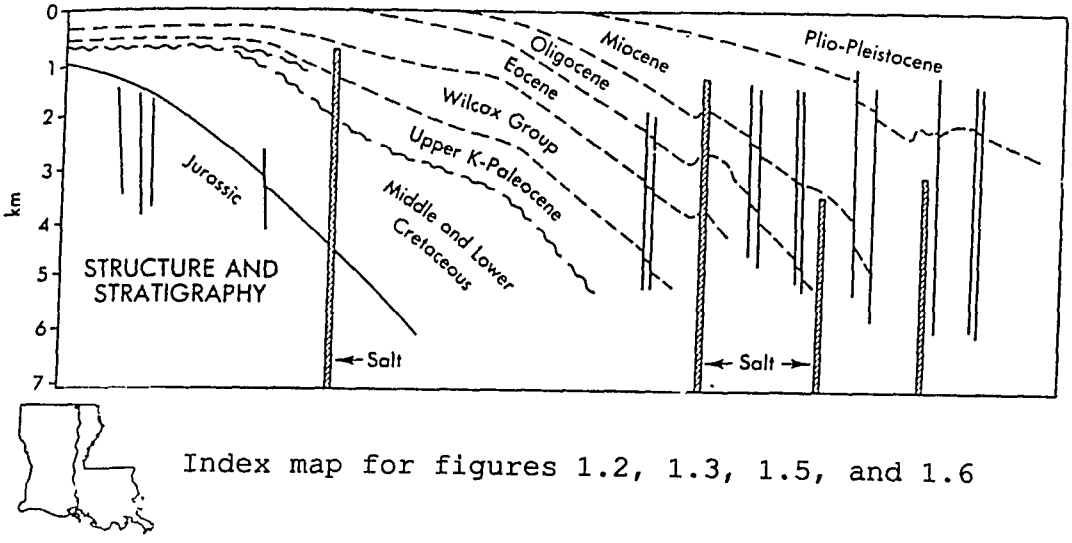
This section describes the general hydrogeology of the Gulf Coast Basin including ground water flow and geochemistry of brines and evaporites. More detailed discussions are given of the hydrogeology and water geochemistry of the alluvial and Wilcox aquifers under subsequent heading. All included material is relevant background discussion to the chapters which follow.

Regional Hydrogeology of the Louisiana Gulf Coast

Sediments of the Louisiana Gulf Coast ranging from Jurassic to Holocene in age are shown in generalized cross-section in figure 1.2. Approximately the southern half of the cross-section, corresponding to the location of the Gulf Coast Salt Basin, shows the presence of salt diapirs, growth faults, and gulfward thickening of Cenozoic sediments. A generalized representation of lithofacies in cross-section is shown in figure 1.3. Selected tectonic features and salt dome basins of the Gulf Coast region are shown in figure 1.4.

For purposes of this discussion water-bearing sediments in the Louisiana Gulf Coast can be divided into two broad hydrogeologic regimes: (1) sediments containing fresh to brackish water and (2) sediments containing saline water to brine. These two regimes are represented along a generalized cross-section by the location of the 10 g/L isosalinity line (fig. 1.5).

The hydrologic regime containing saline water to brine can be farther subdivided into hydropressured and geopressured (overpressured) regions (fig. 1.6). The location of the geopressured region corresponds to the location of the thickening sequence of shale in the southern part of the Louisiana Gulf Coast. Figure 1.6 also shows lines of equal hydraulic head and the corresponding general sense of ground-water movement. Lines of equal hydraulic



Index map for figures 1.2, 1.3, 1.5, and 1.6

Figure 1.2 Generalized cross-section of Jurassic through Pleistocene sediments (cross-section and index map modified from Hanor and Sassen, 1990). Vertical and near-vertical lines represent faults.

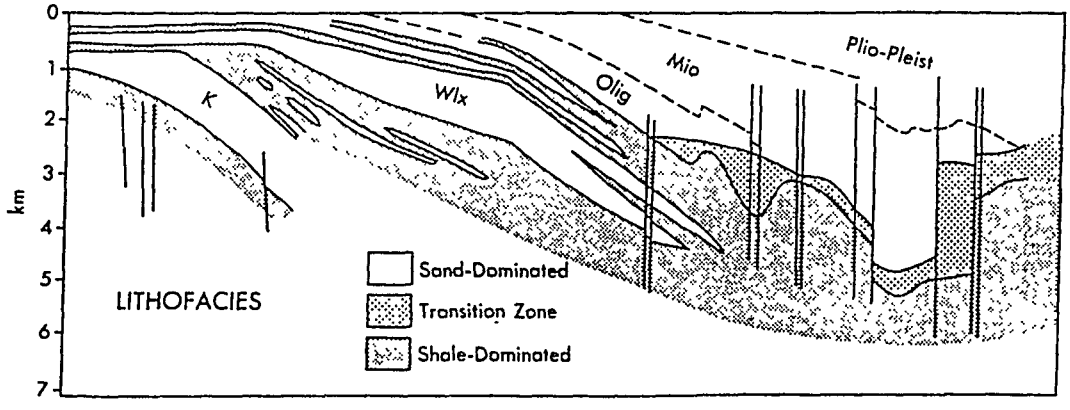


Figure 1.3 Generalized cross-section showing lithofacies of Cretaceous through Pleistocene sediments (modified from Hanor and Sassen, 1990). Vertical and near-vertical lines represent faults.

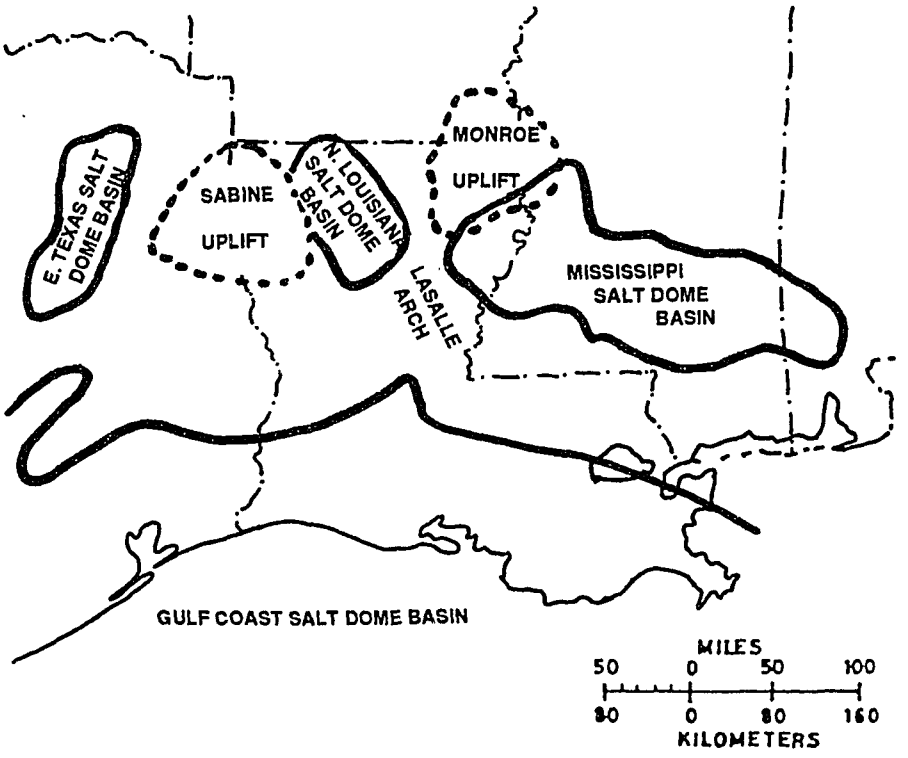


Figure 1.4 Major tectonic and evaporite features of the northern Gulf Coast rim (modified from Holcomb (1971)).

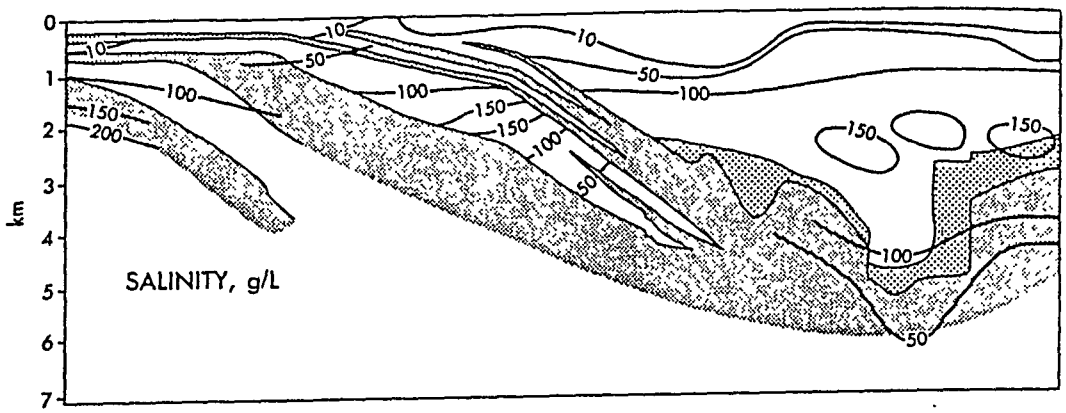


Figure 1.5 Water salinity in Cretaceous through Pleistocene aquifers and confining units (modified from Hanor and Sassen, 1990).

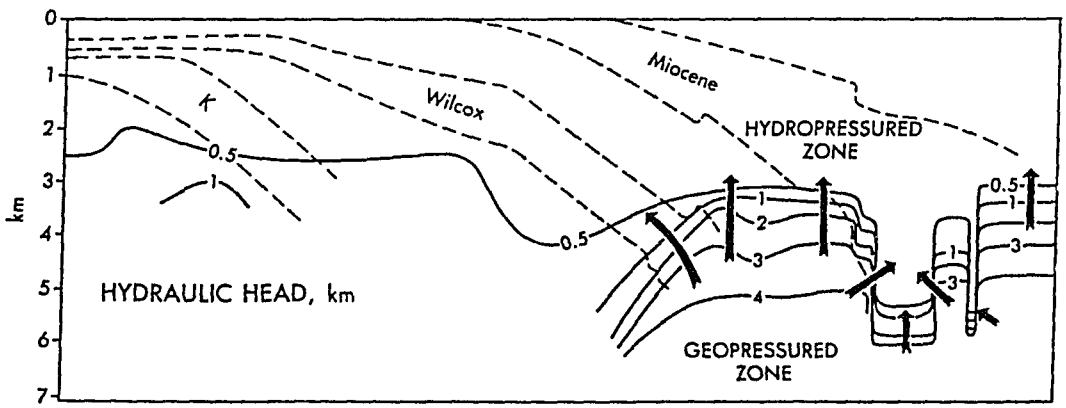


Figure 1.6 Lines of equal hydraulic head and inferred directions of ground-water flow (modified from Hanor and Sassen, 1990).

head were calculated assuming the density of water to be 1000 kg/m^3 (1 g/cm^3). This approach was justified by Hanor and Sassen (1990) on the basis that, in this case, pressure gradients rather than density gradients are the major driving force for subsurface fluid flow.

Potential pathways for fluid migration from the geopressured region into the hydropressured region include faults as well as intercalated sands within the shale sequence separating the two regions. In contrast, Dickey (1988) argued that the shale separating the hydropressured and geopressured regions has sufficiently low permeability to allow no significant cross-formational flow. Hanor and Sassen (1990) counter that the absence of vertical flow out of the geopressured region would cause pressures higher than those observed because of shale dewatering and the thermal expansion of water. Posey and others (1985) have cited isotopic evidence for mixing of pore fluids from the hydropressured and geopressured regions of southern Louisiana requiring fluid flow from the geopressured into the hydropressured region.

Both pressure and density gradients have been theorized to be the driving force for large-scale flow of saline waters and brines in the hydropressured region. Pressure-driven updip lateral flow has been suggested by Hanor and Sassen (1990) and Williamson and others (1990). Stoessell and Moore (1983) and Posey and others (1987) have proposed updip lateral movement of saline waters and brines as a part

of the processes responsible for high Br/Cl-ratio brines in the Smackover Formation in southern Arkansas and for radiogenically-enriched Sr in salt dome materials in southern and central Louisiana, respectively. Density-driven flow has also been suggested to play a major role in the hydrogeology of the Louisiana Gulf Coast. Thermohaline convection, which includes elements of pressure, temperature, and salinity gradients, has been proposed as a major driving force of ground-water flow near salt domes in southern Louisiana (Hanor, 1987; Bennett and Hanor, 1987; and Ranganathan and Hanor, 1988). Hanor (1987) has suggested kilometer-scale movement of ground-water in the hydropressured region is associated with thermohaline convection.

Geochemistry of Brines and Salt

Geochemistry of Brines

Relatively little data exists on the composition of brines in Tertiary sediments in central Louisiana. Available data include the studies of Hawkins and others (1963) and Collins (1970). Brines and saline waters in the Wilcox aquifer of central Louisiana are of a Na-Cl type, are depleted in K, Mg, and Br, and are enriched in Sr relative to seawater evaporated to equal salinity. Ca concentrations are more variable but, in the majority, show higher

concentrations than expected in seawater evaporated to equal salinity (Collins, 1970).

Brines and saline waters in both the hydropressured and geopressured zones of coastal Louisiana, Mississippi, and Texas have been more thoroughly studied. The first systematic collection and analyses of brines from east Texas were those of Hawkins and Pearson (1964). These were followed by the first isotopic analyses of Gulf Coast brines by Clayton (1966).

Collins (1974) presented the first widely-available chemical data documenting the presence of high-Br brines in the Jurassic Smackover Formation of southern Arkansas. The data of Collins (1974) also established a high Br content (mean value of 240 mg Br/kg halite) for the Louann Salt underlying the Smackover Formation in southern Arkansas. Carpenter and Trout (1978) argued that the majority of Br in Smackover brines had a source other than evaporation of seawater. The consensus from the literature is that high Br brines present in the Smackover Formation have been post depositionally introduced. From this point onward opinions vary. Stoessell and Moore (1983) have argued for Br enrichment of Smackover brines by incongruent dissolution and recyrstallization of halite followed by updip migration of the resulting brines. They also suggested illite formation and sylvite dissolution as factors determining the composition of Smackover brines. Hanor (1987, p. 81-83) suggested a rather complex process involving dissolution of

sylvite or carnallite and concurrent precipitation of halite in the Louann Salt followed by vertical emplacement of the resulting fluids into the Smackover Formation. Moldovanyi and Walter (1992) argue for Br enrichment of Smackover brines by recrystallization of the underlying Louann Salt followed by vertical emplacement of the resulting fluids. Vertical emplacement is supported by the work of Stueber and others (1984) who cite Sr isotope evidence for the origin of Smackover brines in the underlying Louann salt.

Carpenter (1974) described the occurrence of metal-rich brines in sediments of Jurassic and lower Cretaceous ages in central Mississippi. Carpenter (1978) subsequently argued that these metal-rich brines originated as interstitial fluids in evaporite sediments followed by further alteration of the brines during burial diagenesis. Diagenetic changes included Ca enrichment by dolomitization of calcite, Sr enrichment by recrystallization of Sr-rich anhydrite, and depletion of SO_4 by microbial action or precipitation of anhydrite. K and Na were lost from solution by conversion of kaolinite to illite or K-feldspar and by albitization of plagioclase or kaolinite, respectively. Subsequent study of the stable isotopes of O and H confirm the contribution of bittern waters to these metal-rich brines (Kharaka and others, 1987).

The origin of brines in the lower Cretaceous Edwards Group in south central Texas has been discussed by Land and Prezbindowski (1981). They argue for subsurface dissolution

of halite followed by reaction of Na with plagioclase to produce authegenic albite and a brine enriched in Na, Ca, and Cl. Dedolomitization and precipitation of authegenic calcite was suggested to account for an updip increase in dissolved Mg/Ca. Land and Prezbindowski (1981) also advanced the idea that brines may become enriched in Br by recrystallization of halite. This mechanism of Br enrichment has also been used to explain elevated Br/Cl ratios in brines hosted by sediments in offshore Louisiana (Land and others, 1988).

The origin and geochemistry of geopressured brines in Oligocene Frio sediments along the Texas Gulf Coast has been studied by Morton and Land (1987). Geochemical characteristics of Frio brines are determined by the extent of mixing between three end-member waters: (1) an NaCl-dominated brine formed by subsurface dissolution of halite, (2) an acetate-rich water derived from the geopressured zone, and (3) a Ca-rich water derived form underlying Mesozoic strata. Workman and Hanor (1985) have also discussed the presence of acetate-bearing water, presumably derived from geopressured sediments, in brines hosted by Tertiary sediments in south central Louisiana.

Isotopes of Sr, O, and H in Gulf Coast brines have been studied by Posey and others (1985) and Russell and others (1988). In both studies dissolved Sr generally increased with depth and the range of $^{87}Sr/^{86}Sr$ ratios were typically unique to a given oil field. Russell and others (1988)

suggested that brines were enriched in radiogenic Sr as a result of dissolution of carbonate phases or other unstable minerals in adjoining shales. Based on isotopes of Sr, O, and H, Posey and others (1985) identified brines above 2000 m depth which had partially equilibrated with terrigenous clastic rocks. Brines below 2000 m depth were a result of mixing of Oligocene/Miocene seawater with water derived from the geopressured zone. Recent work by Chaudhuri and Clauer (1993) emphasized the importance of alteration and dissolution of alkali feldspars and mica and illitization of smectite in determining the $^{87}Sr/^{86}Sr$ ratio of subsurface brines and saline waters from a number of sedimentary hydrogeologic settings.

Geochemistry of Salt

The Jurassic Louann Salt is generally accepted to be the mother salt from which salt domes and diapirs throughout the Gulf Coast originate. Subsurface dissolution or recrystallization of halite has been advanced by many authors (Hanor, 1987; Bennett and Hanor, 1987; Stoessell and Moore, 1983; Land and Prezbindowski, 1981; Morton and Land, 1987; and Land and others, 1988) as an important source of salinity for Gulf Coast brines. Geochemical analyses of Louann material obtained from shallow diapirs and domes yield Br concentrations ranging from 17 to 290 mg/kg with most samples containing about 50 mg/kg (Land and others,

1988). A Br concentration of less than 60 mg/kg is consistent with first precipitation of marine halite. Br concentrations of approximately 200 mg/kg are consistent with coprecipitation of halite with bittern salts (Hostler, 1979). A more complex scenario involving recrystallization of halite in the presence of Br-rich brines has been advanced by Land and others (1988) to explain halite having Br concentrations of approximately 200 mg/kg.

Extensive work has been done on the isotopes of Sr in salt-dome material and their use as indicators of water-rock interaction. The $^{87}Sr/^{86}Sr$ ratio of mid-Jurassic seawater was approximately 0.7069 to 0.7071 (Burke and others, 1982). Sr in samples of Louann-derived halite from coastal Louisiana, coastal Texas and northern Mexico are typically more radiogenic than mid-Jurassic seawater (Posey and others, 1987; Land and others, 1988). In addition, a sample of Louann material from southern Arkansas has a reported $^{87}Sr/^{86}Sr$ ratio of 0.70808 (Stueber and others, 1984). Sr more radiogenic than mid-Jurassic seawater in Louann-derived halite is though to result from interaction of deforming or recrystallizing halite and a brine or brines enriched in radiogenic Sr (Land and others, 1988).

Meaningful concentrations of Sr are present as celestite and strontianite in salt-dome cap rocks in the Mississippi Salt Dome Basin (Walker, 1974; Saunders and others, 1988) and at Vacherie Dome in Louisiana (Rovik, 1978). Saunders and others (1988) reported that dark banded

calcite contained up to 50% celestite and strontianite having $^{87}Sr/^{86}Sr$ ratios ranging from 0.7077 to 0.7081. Sr is also present in salt-hosted and cap-rock anhydrite as well as cap-rock calcite. Werner and others (1988) reported an $^{87}Sr/^{86}Sr$ ratio of 0.7068, essentially the same as mid-Jurassic seawater, for anhydrite from the Richton Dome cap rock in central Mississippi. In contrast, Land and others (1988) report $^{87}Sr/^{86}Sr$ ratios of 0.7067 to 0.7086 for anhydrite from salt domes in northern Mexico. Land and others (1988) noted a decrease in $^{87}Sr/^{86}Sr$ with increasing depth to a ratio essentially that of mid-Jurassic seawater and hypothesized that radiogenic Sr in shallower anhydrite resulted from interaction with a radiogenic-Sr rich brine. Posey and others (1987) report the occurrence of anhydrite, barite, and celestite having $^{87}Sr/^{86}Sr$ ratios more radiogenic than that of mid-Jurassic seawater for salt domes and diapirs in the Gulf Coast Salt Basin and for Winnfield Dome in the North Louisiana Salt Basin. Ratios of $^{87}Sr/^{86}Sr$ in salt-dome materials in other areas of the North Louisiana Salt Basin are consistent with mid-Jurassic seawater.

A consensus seems to exist that not enough ^{87}Rb is present in salt-dome materials to account for observed amounts of radiogenic Sr. An external radiogenic-Sr rich brine which has interacted with clastic sediments is typically called upon to supply the required radiogenic Sr. The history of water-rock interactions in the salt-dome environment appears to be complex in both time and space. In

general, salt-dome materials in the Gulf Coast Salt Basin of coastal Louisiana and northern Mexico contain $^{87}Sr/^{86}Sr$ ratios more radiogenic than mid-Jurassic seawater. The Mississippi Salt Basin contains some salt-dome materials which are enriched in radiogenic Sr and some which are not. With the exception of Winnfield Dome, the North Louisiana Salt Basin contains salt-dome materials which have $^{87}Sr/^{86}Sr$ ratios consistent with mid-Jurassic seawater. In addition to the spatial complexity of the distribution of Sr isotopes, Posey and others (1987) suggest that five separate intervals of water-rock interaction have taken place in the salt-dome environment of the Gulf Coast.

Less work has been done on the stable isotopes of oxygen in salt dome/diapir materials in the Gulf Coast Region. Werner and others (1988) found average $\delta^{18}O$ values of +11.6 o/oo in caprock anhydrite and +25.6 o/oo in caprock calcite from Richton Dome in the Mississippi Salt Dome Basin. Prikryl and others (1988) reported $\delta^{18}O$ values ranging from +25.9 to +23.0 o/oo in caprock calcite from the Damon Mound Salt Dome in the Gulf Coast Salt Dome Basin.

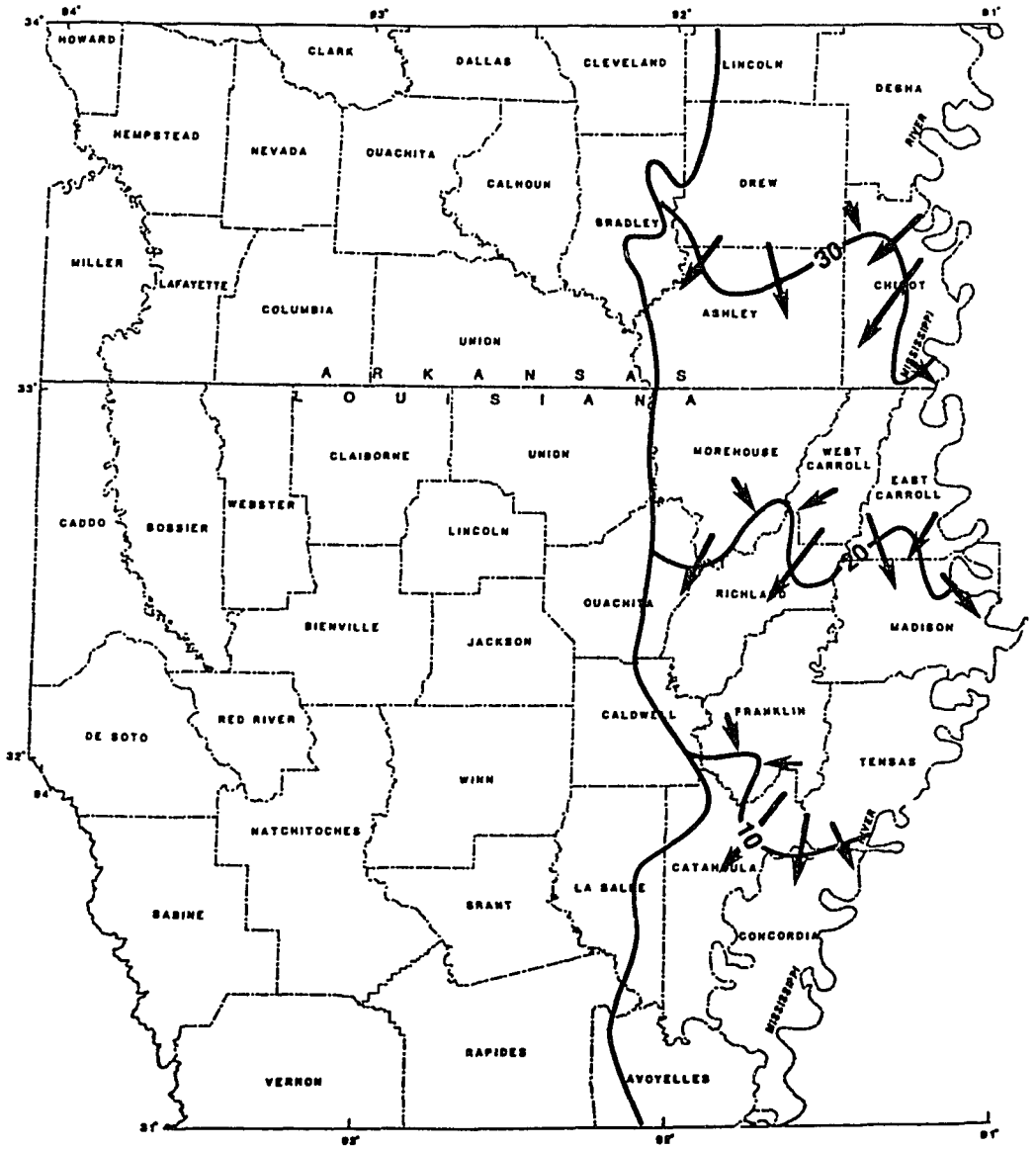
REGIONAL HYDROGEOLOGY OF THE ALLUVIAL AQUIFER

The uppermost 24 to 61 m (80 to 200 ft) of clay, silt, sand, and gravel deposited by the Mississippi and smaller rivers within the Mississippi River Valley collectively forms the Mississippi River Valley alluvial deposits. The

alluvial deposits generally thicken southward and toward the present position of the Mississippi River. The top approximately 12 m (40 ft) of alluvial deposits are primarily silt and clay of Holocene age. Pleistocene sand and gravel make up the remainder of the alluvial deposits and form the Alluvial Aquifer. Below depths of approximately 12 m (40 ft), alluvial deposits systematically coarsen with depth. Gravel up to 7.5 cm (3 in) in diameter is common in basal deposits. The base of the alluvial deposits is marked by the deepest occurrence of Pleistocene gravel (Whitfield, 1975).

Rainfall is the largest source of recharge to the Alluvial Aquifer (Whitfield, 1975). The Alluvial Aquifer is also recharged by up to 1.3 cm/yr (0.5 in./yr) of upward flow (Ackerman, 1989). Lateral flow of water in the Alluvial Aquifer of north Louisiana is generally southward (fig. 1.7). Water not pumped from the Mississippi River Alluvial Aquifer discharges into major rivers and streams in the Mississippi River alluvial valley (Whitfield, 1975; Ackerman, 1989).

Ca and HCO_3 are generally the major cation and anion, respectively, in alluvial water where Cl concentrations are less than approximately 250 mg/L. In parts of Richland Parish, Louisiana, Na is the major cation (Whitfield, 1975). Whitfield (1975) and Smoot (1986) have mapped ares of the Alluvial Aquifer in Franklin, Richland, and Madison



LINE OF EQUAL HYDRAULIC HEAD IN METERS ABOVE SEA LEVEL

GENERALIZED DIRECTION OF LATERAL GROUND-WATER FLOW

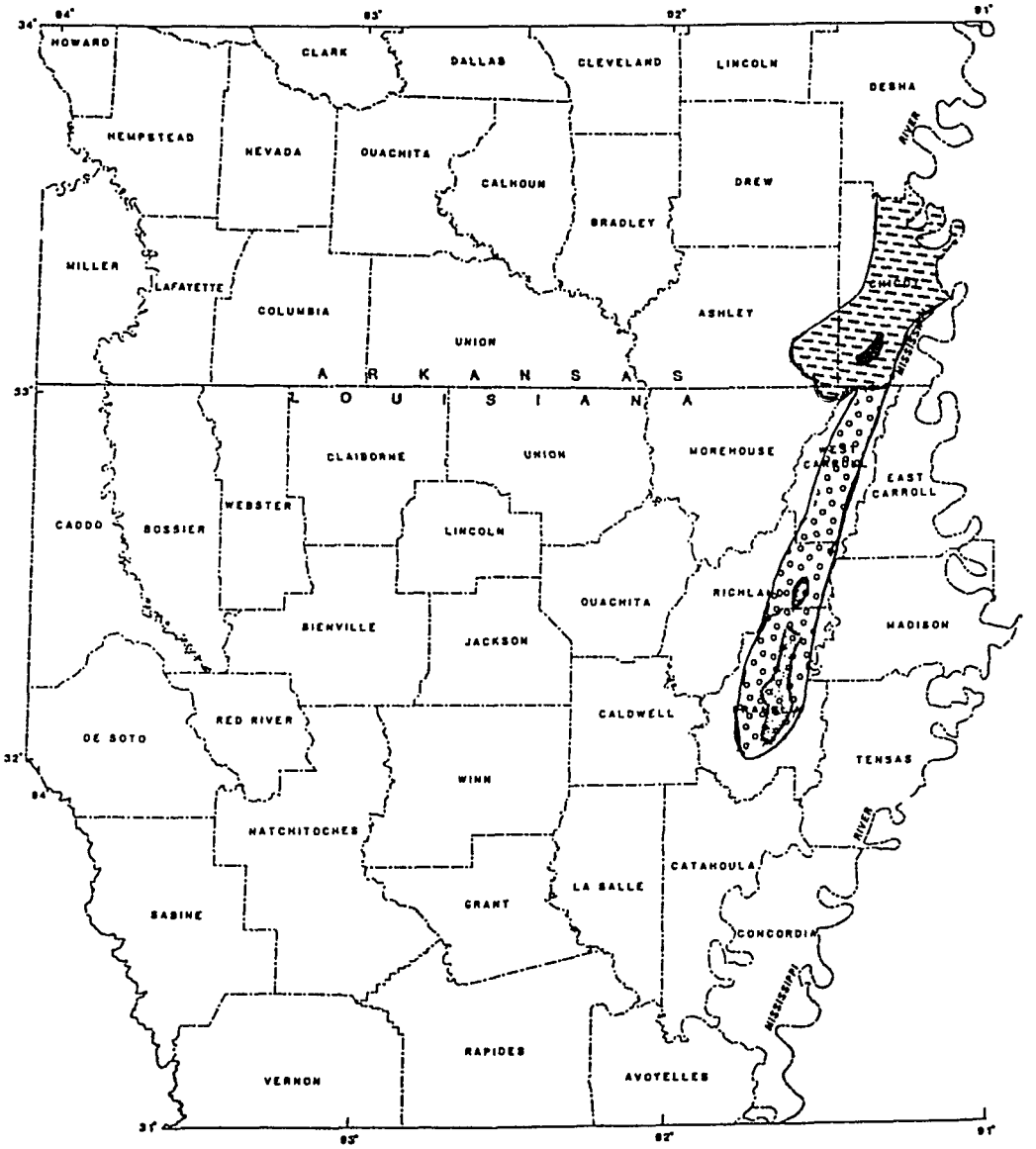
Figure 1.7 Areal extent of, hydraulic head in, and generalized directions of lateral ground-water flow in the Mississippi River Alluvial Aquifer (modified from Whitfield, 1975 and Ackerman, 1989).

Parishes, Louisiana which contain only water with Cl concentrations of approximately 250 mg/L or greater.

Areas of the Alluvial Aquifer in Richland and Franklin Parishes, Louisiana which contain only water with Cl concentrations of approximately 250 mg/L or greater are included in a band of ground water extending northeast from Franklin through Richland and West Carroll Parishes, Louisiana which contains Cl concentrations of 100 mg/L or greater (Whitfield, 1975). This band continues into southern Arkansas as an area of ground water containing dissolved solids concentrations of 500-1,000 mg/L (Boswell and others, 1968) (fig. 1.8). Upward flow has been suggested as the source of elevated concentrations of dissolved solids in the band of ground water containing 100 mg/l or greater Cl and 500-1,000 mg/L dissolved solids (Whitfield, 1975; Fitzpatrick, 1985). An area of alluvial water having anomalously elevated salinity, (>1,000 mg/L) (Boswell and others, 1968) exists in southern Chicot County, Arkansas (fig. 1.8).

REGIONAL HYDROGEOLOGY OF THE WILCOX AQUIFER

The Wilcox Group consists of a series of terrigenous siliciclastic sediments of Eocene-Paleocene age. Wilcox sediments were derived from northern and northeastern source areas and deposited along the Gulf Coast by the ancestral Red and Mississippi Rivers as a series of deltaic



500 - 1,000 MG/L DISSOLVED SOLIDS

>1,000 MG/L DISSOLVED SOLIDS

100 - 250 MG/L CHLORIDE

>250 MG/L CHLORIDE

Figure 1.8 Band of elevated salinity in alluvial water (modified from Boswell and others, 1968 and Whitfield, 1975).

depocenters, separated by interdeltaic lagoons, bays, and strandplains. Wilcox Group sediments are present in Mississippi through Louisiana into eastern Texas and northward into central Arkansas (Echols and Malkin, 1948; Fisher and McGowen, 1967; Galloway, 1968; Lowry, 1987; and Tye and others, 1991).

The term Wilcox aquifer as used here collectively refers to all water-bearing sands within the Wilcox Group. Following the lead of Hosman and others (1968), Williamson and others (1990) have subdivided the Wilcox aquifer into lower, middle, and upper units corresponding to the lower fluvial-dominated deltaic depocenter, the middle marine transgressive unit, and the upper wave-dominated deltaic depocenter of the Wilcox Group as described by Galloway (1968) and Lowry (1987). For the purposes of this dissertation the hydrologic nomenclature of Hosman and others (1968) and Williamson and other (1990) will be used in discussing the Wilcox aquifer.

A variable-density ground-water flow model was used by Williamson and others (1990) to simulate flow in Gulf Coast aquifers including the Wilcox aquifer of northern and central Louisiana, eastern Texas, southern and central Mississippi, and southern Arkansas. Subsurface salinities were calculated using data from SP logs as discussed by Weiss (1987). Ground water densities were calculated using bottom-hole temperatures taken from selected electric logs

covering the study area and hydrostatic pressure corresponding to the center of a model block.

The variable-density ground-water flow model of Williamson and others (1990) was discritized into 17 layers. Fifteen of these layers represent aquifers and confining units which are areal to subareal in extent throughout the Mississippi River Embayment. Individual model blocks in which flow calculations were performed were 10 mi. per side (100 $mi.^2$ per block). The Midway confining unit at the base of the Wilcox aquifer was taken as a no flow boundary at the base of the model where hydropressured conditions existed to the top of the Midway. Where geopressured conditions existed above the top of the Midway (commonly down-dip), the top of the geopressured zone was taken as a no flow boundary. Although, as has been argued earlier, flow likely does occur between the geopressured and hydropressured zones, the amount of such flow was assumed to be insignificant to the overall water budget of the regional model.

Net recharge rates over the area of the regional model were, at best, poorly known. As such, net recharge was calculated by assuming the presence of a constant-head layer at the top of the regional model. The volume of flow into the model as surficial recharge was calculated based on the differences in head between the uppermost model layer and the constant-head layer. This technique of estimating recharge required an arbitrary assignment of hydraulic conductivity between the uppermost model layer and the

constant-head layer. The numerical algorithm used in the model of Williamson and others was described by Kuiper (1983; 1985).

Lateral and vertical directions of ground-water flow for the Wilcox aquifer from the simulation of Williamson and others (1990) are shown in figures 1.9, 1.10, and 1.11. Lateral flow in the lower unit of the Wilcox aquifer is generally updip in central and northern Louisiana. Lateral flow in southern and central Mississippi is east to west away from the eastern recharge area of the Wilcox aquifer. Lateral flow in southern Arkansas is northwest to southeast. Lateral flow in the lower unit of the Wilcox aquifer generally converges in the area of the Monroe Uplift. Lateral flow in the middle unit of the Wilcox aquifer is south to north in central Louisiana, west to east in eastern Texas, and east to west in southern and central Mississippi. Eastward and westward flow directions converge in northern Louisiana. As is the case in the lower unit, lateral flow in northern Louisiana, southern Arkansas, and central Mississippi converges in the area of the Monroe Uplift. Lateral flow in the upper unit of the Wilcox aquifer follows basically the same pattern as is present in the middle unit with the exception that northwest to southeast flow dominates in central Louisiana.

Because the contact between the Midway confining unit and the Wilcox aquifer was simulated as a no-flow boundary by Williamson and others (1990), no net vertical flow

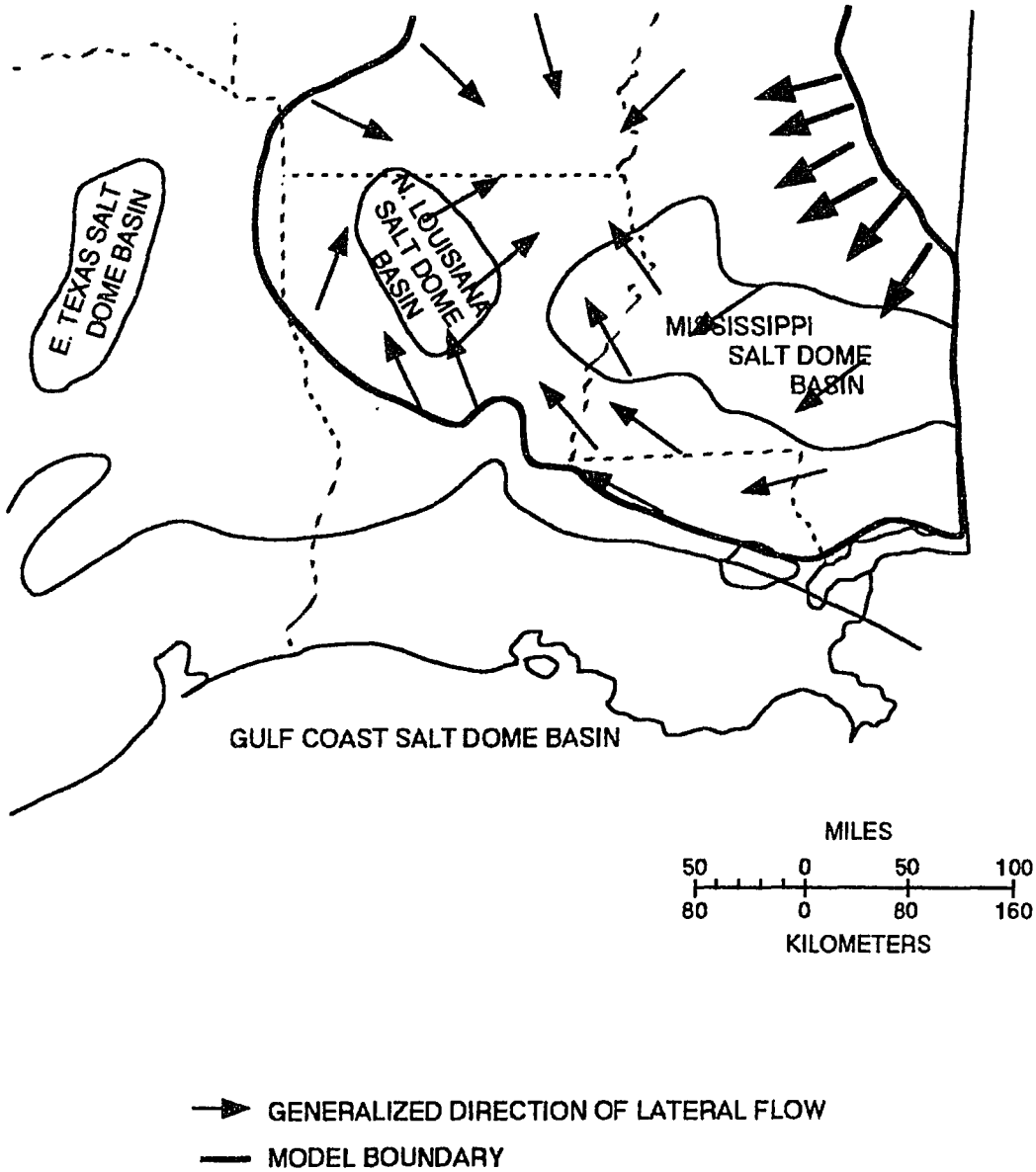


Figure 1.9 Lateral ground-water flow directions in the lower unit of the Wilcox Aquifer. Flow directions modified from Williamson and others (1990). Base map modified from Holcomb (1971).

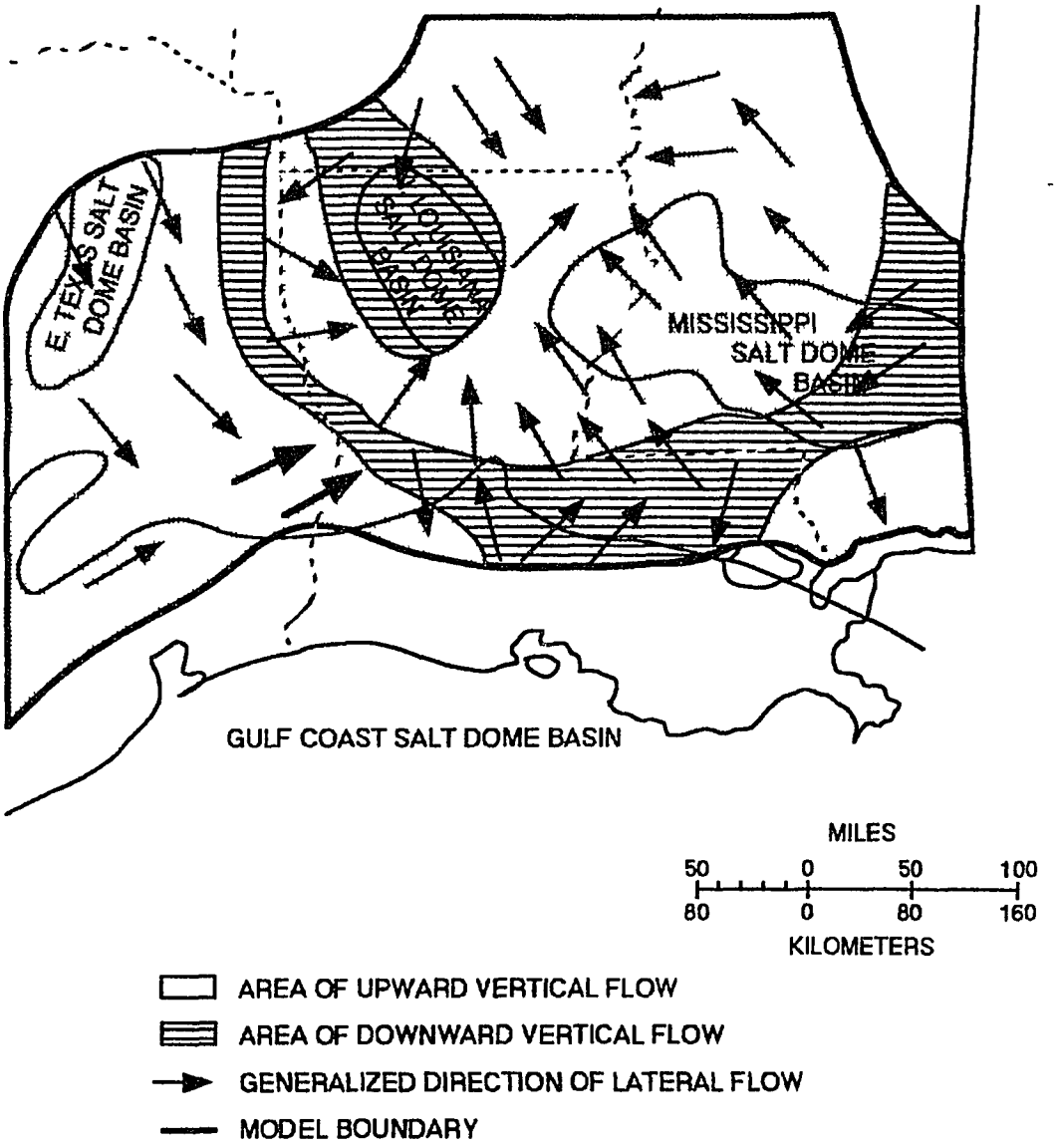


Figure 1.10 Lateral and vertical ground-water flow directions in the middle unit of the Wilcox Aquifer. Flow directions modified from Williamson and others (1990). Base map modified from Holcomb (1971).

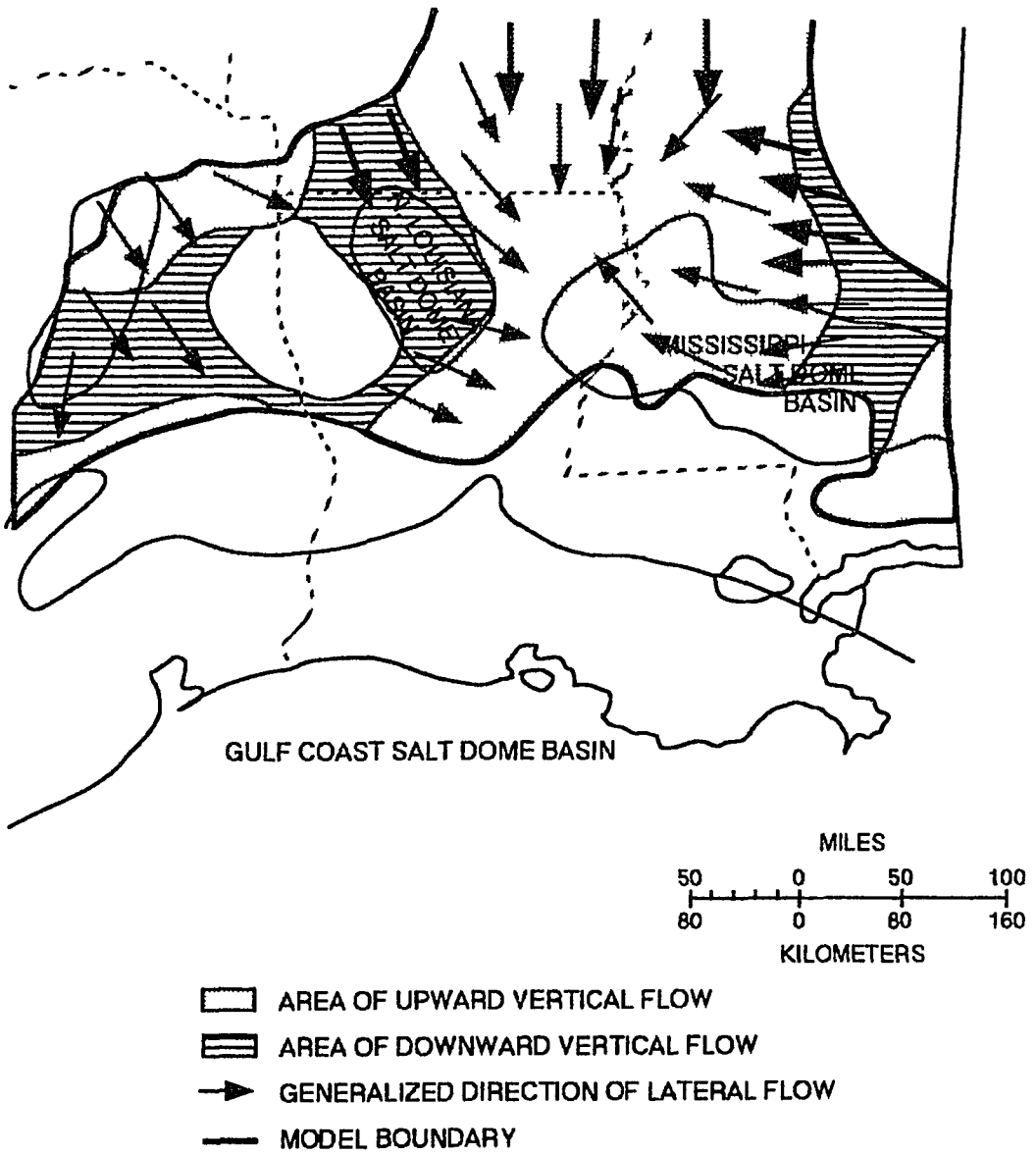


Figure 1.11 Lateral and vertical ground-water flow directions in the upper unit of the Wilcox Aquifer. Flow directions modified from Williamson and others (1990). Base map modified from Holcomb (1971).

direction was calculated for the lower unit of the Wilcox aquifer. Vertical flow is generally upward from the lower into the middle unit of the Wilcox aquifer. Downward flow exists in the area of the North Louisiana Salt Dome Basin and in an arcuate band from eastern Texas through southern Louisiana and into southern Mississippi. Vertical flow is upward from the middle into the upper unit of the Wilcox aquifer throughout most of northern Louisiana, southern Arkansas, and western Mississippi. Downward flow is present in eastern Texas and northwestern Louisiana including the North Louisiana Salt Dome Basin, the southern half of the East Texas Salt Dome Basin, and surrounding the Sabine Uplift. A smaller area of downward flow is present in southeastern and east central Mississippi.

Funayama (1990) concluded that salinity in Wilcox pore fluids of central Louisiana was derived from dissolution of evaporites in the North Louisiana and Gulf Coast Salt Dome Basins. These sources of salinity implied that solutes in the Wilcox aquifer have been transported to present-day locations by lateral migration exceeding 100 km.

CHAPTER II

BRACKISH WATER IN THE ALLUVIAL AQUIFER AND THE JASPER AQUIFER SYSTEM IN SOUTH CENTRAL CONCORDIA PARISH

PURPOSE

Determining the source of brackish water in otherwise freshwater aquifers can have important environmental, economic, and legal ramifications. The purpose of this chapter is to demonstrate the use of Br, Cl, and the isotopes of Sr in determining the source(s) of solutes in brackish water in the Alluvial Aquifer of the study area.

Various geochemical tracers have been used to investigate sources of salinity in freshwater aquifers (Leanord, 1964; Leanord and Kleinschmidt, 1976; Magaritz and others, 1981; and Whittemore, 1983). The use of tracers which do not behave conservatively, such as the ratios of major cations to chloride, can often lead to difficult and non-unique interpretations of collected data. A fuller discussion of the tracers used and some of the problems associated with them appears in Appendix I. The conservative nature of Br and Cl ions and the $^{87}Sr/^{86}Sr$ ratio in many hydrogeologic environments holds promise for developing techniques for solute tracing in freshwater environments which are relatively inexpensive and straightforward.

DESCRIPTION OF THE STUDY AREA

The part of south central Concordia Parish between Monterey and Deer Park, Louisiana containing sampled irrigation and monitor wells and plugged and abandoned oil wells covers approximately 23 km^2 (9 mi^2) (figs. 1.1 and 2.1.). All references to study area in this chapter refer to this part of Concordia Parish (defined as the subset of the Concordia Parish study area in figure 1.1) unless otherwise specified.

The geohydrologic column representing the entire Concordia Parish study area including the Wilcox and younger aquifers and confining units is shown in figure 2.2. Land surface within the study area has a mean elevation of approximately 15 m (50 ft) above sea level and very little topographic relief. Agriculture is the primary land use. Irrigation using alluvial water began in 1976 and continued until 1982 when salinity of irrigation water began to cause damage to irrigated crops (Lee Bean, Angelina Plantation Farms, personal communication, 1988).

HYDROGEOLOGY OF THE ALLUVIAL AQUIFER

The Mississippi River alluvial sediments unconformably overlie Miocene sediments of the Carnahan Bayou member of the Fleming formation throughout the entire Concordia Parish study area. Pleistocene Mississippi River alluvial sediments

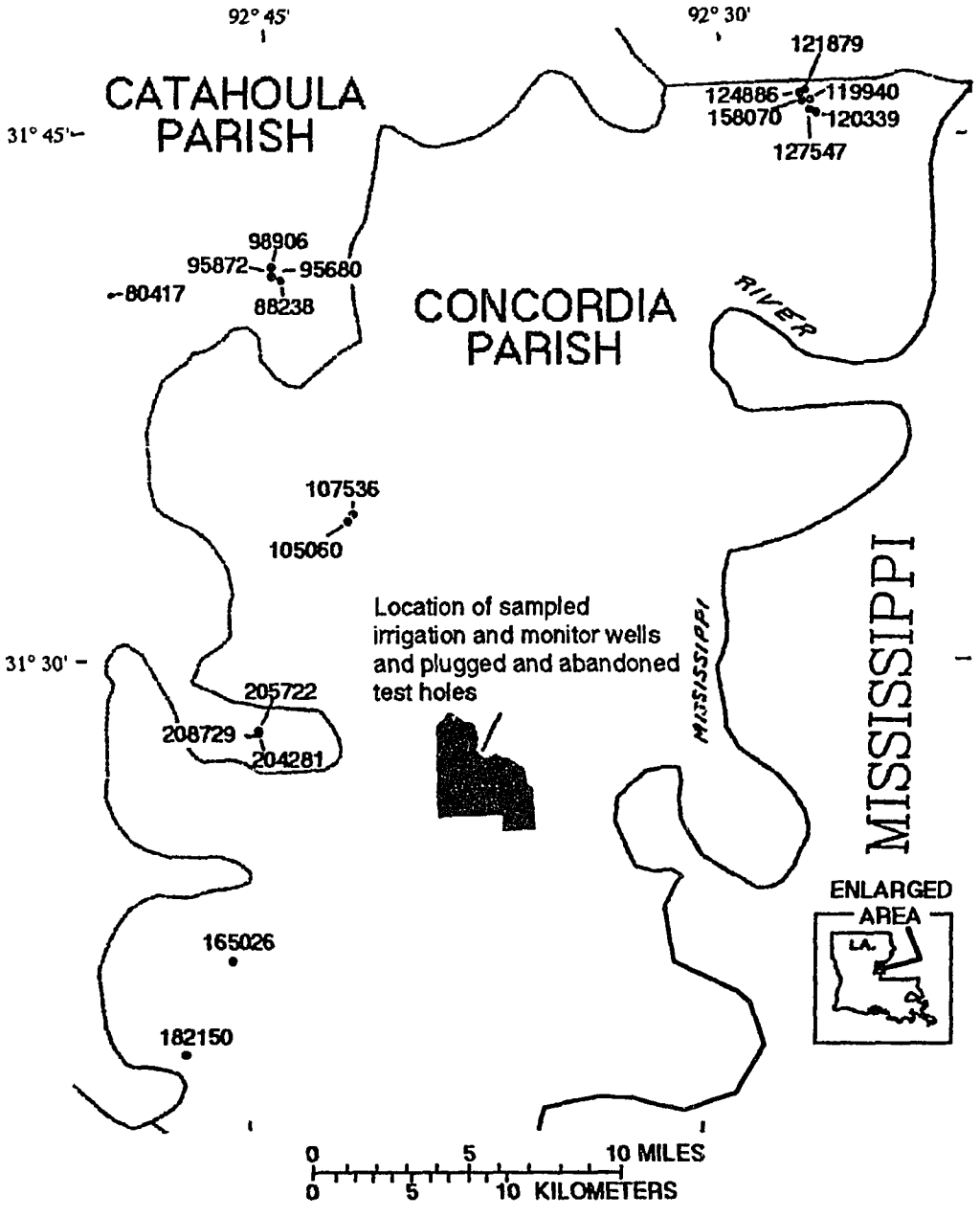


Figure 2.1 Location of the subset of the Concordia Parish study area containing sampled irrigation, monitor, and plugged and abandoned oil wells and test holes and the location of sampled oil wells in the Concordia Parish study area.

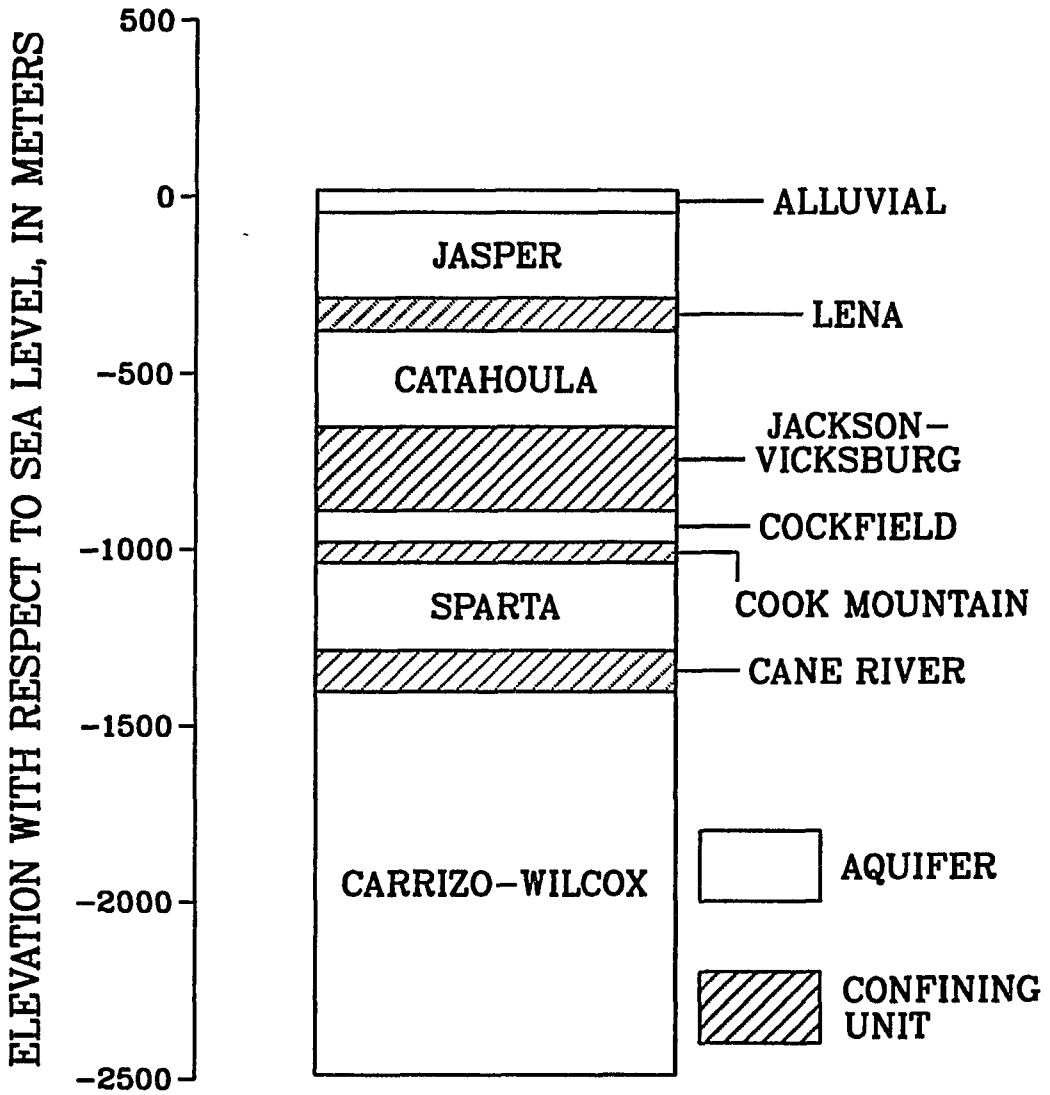


Figure 2.2 Generalized geohydrologic column showing the Wilcox and younger aquifers and confining units in the Concordia Parish study area (modified from Eversull, 1984).

form the Alluvial Aquifer. Miocene Carnahan Bayou sediments of the Fleming Formation form the Jasper aquifer system.

The thickness of the Alluvial Aquifer ranges from approximately 43 m (140 ft) in the northern part of the study area to approximately 55 m (180 ft) in the southern part. The base of the Alluvial Aquifer is marked by the deepest occurrence of Pleistocene gravel (Whitfield, 1975). The Jasper aquifer system is approximately 245 m (800 ft) thick within the study area. The base of the Jasper aquifer system within the study area is marked by the clays of the Lena confining unit.

Insufficient water-level data exist to directly evaluate directions of ground-water flow in the Alluvial Aquifer in Concordia Parish, Louisiana. It is probably safe to assume, however, that ground water flows generally southward and discharges into major rivers and streams as has been documented for the Alluvial Aquifer in Tensas Parish which lies directly to the north of Concordia Parish (Whitfield, 1975).

Water in the Alluvial Aquifer of Concordia Parish is generally a Ca-HCO_3 type. Concentrations of hardness typically range from 200 to 400 mg/L as $CaCO_3$ and concentrations of Cl typically range from 10 to 20 mg/L in the study area (Whitfield, 1975).

DATA COLLECTED

Seven irrigation wells and six monitor wells located in the study area and screened in the Alluvial Aquifer or the uppermost part of the Jasper aquifer system were sampled between 1988 and 1989 (fig. 2.3). Irrigation wells were typically screened over intervals of up to 12 m (40 ft) and could produce a mixture of subsurface waters from a density-stratified system. Thus, the concentration of any constituent present in water produced from irrigation wells does not necessarily reflect the highest concentration present in the aquifer. Monitor wells were typically screened over a 3 m (10 ft) interval and produced water more characteristic of in-situ conditions. Results of chemical analyses of ground-water samples taken from these wells are given in table 2.1. All of the monitor wells are screened in the uppermost part of the Jasper aquifer system with the exceptions of well Co-205, which is screened in the Alluvial Aquifer, and well Co-43, which is screened near the base of the Jasper aquifer system. Well Co-43 is located approximately 1.6 km (1 mi) west well Co-114.

Samples of saline waters and brines were collected from 18 oil wells in the entire Concordia Parish study area between 1988 and 1989 (fig. 2.1). All sampled oil wells were screened within the Wilcox aquifer. Results of chemical analyses of saline waters and brines are shown in table 2.2.

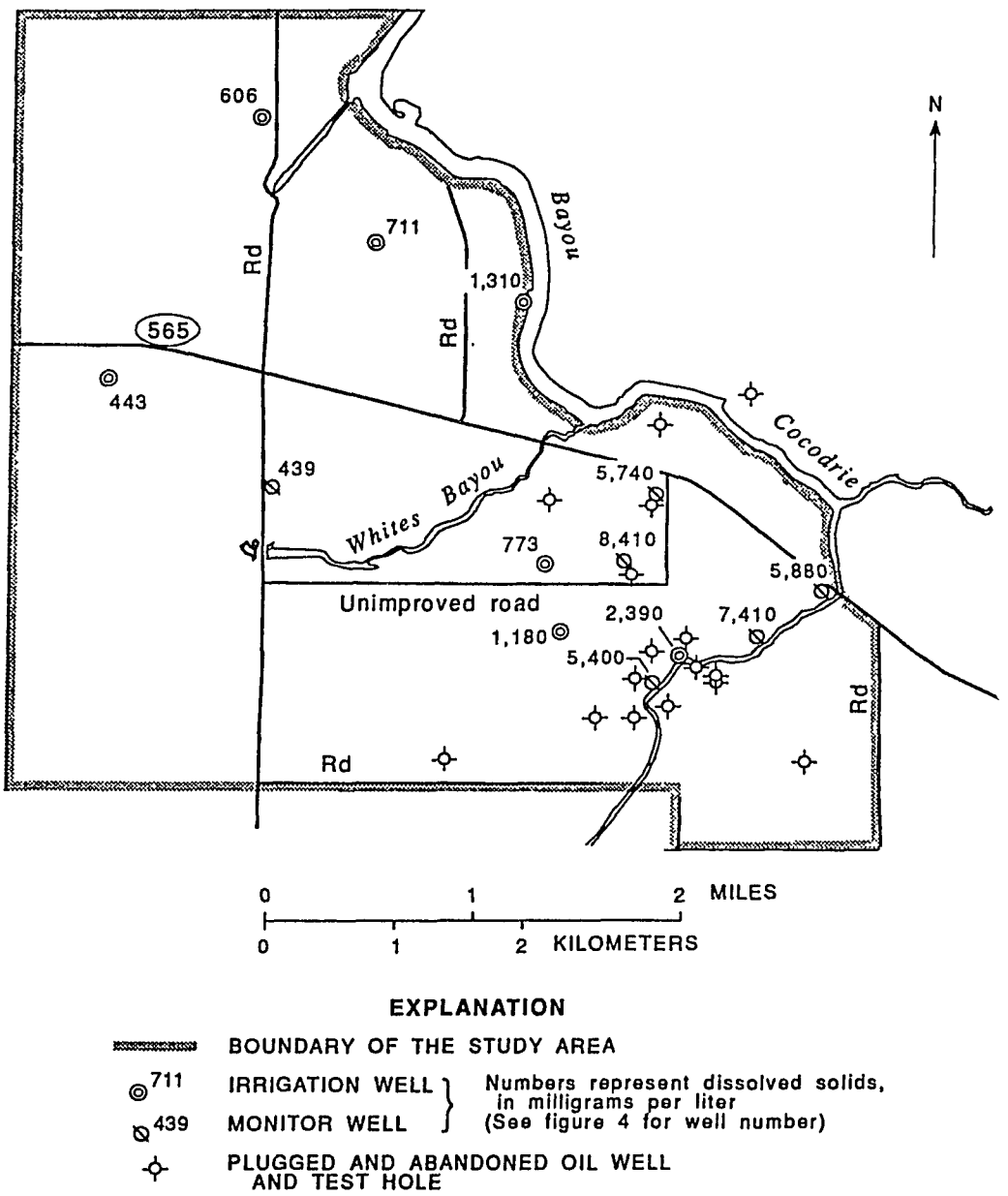


Figure 2.3 Locations of irrigation, monitor, and plugged and abandoned oil wells and test holes.

Table 2.1 Chemical analyses of brackish and fresh waters from irrigation and monitor wells in Concordia Parish.

Well Number	Depth in m below sea level	Sample Date (YY-MM-DD)	Temp. (°C)	Specific Conductance (µS/cm @ 25°C)	pH	Alkalinity (mg/L HCO3)	Ca (mg/L)	Mg (mg/L)	Ba (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO4 (mg/L)	SiO2 (mg/L)	Sr (mg/L)	Br (mg/L)	Dissolved Solids (mg/L)	87Sr/86Sr
Co-43	196.3	67-09-26	23.5	2720	7.4	- -	16	3.7	- -	570	4.7	670	< 1.0	42	- -	- -	1490	- -
Co-114	29.9	88-08-17	21.0	770	7.1	380	82	30	0.18	36	1.4	52	18	38	0.23	0.1	443	- -
Co-115	25.3	88-09-01	20.0	2120	7.1	493	160	48	0.80	200	7.3	450	1.5	39	0.50	0.6	1180	- -
Co-119	23.8	88-09-02	20.0	2400	7.2	488	110	34	0.60	340	5.7	550	2.2	33	0.52	1.3	1310	- -
Co-120	23.8	88-08-18	20.0	1180	7.1	536	120	44	0.63	74	3.7	84	97	40	0.30	0.2	711	- -
Co-122	23.8	88-08-19	22.0	1020	7.1	546	120	34	0.45	57	7.5	50	42	43	0.58	0.1	606	- -
Co-177	24.4	88-08-18	21.0	1530	7.3	575	140	46	0.64	110	6.6	230	1.7	40	0.68	0.3	773	- -
Co-178	24.4	88-08-15	22.0	4220	6.9	356	180	57	1.7	590	10	1100	1.0	30	0.74	1.7	2390	- -
Co-200	44.8	89-07-25	21.0	11000	7.3	368	180	46	2.7	1800	17	3100	< 1.0	36	7.7	3.6	5880	0.70818
Co-201	48.8	89-07-25	21.0	10000	7.2	347	280	71	1.8	1600	16	3000	< 1.0	31	4.9	3.5	5740	0.70831
Co-202	57.0	89-07-25	21.0	14000	7.1	324	310	75	1.8	2500	24	4400	< 1.0	36	13	5.6	8410	0.70814
Co-203	56.4	89-07-27	21.0	13000	7.0	341	280	70	4.5	2100	18	3900	< 1.0	35	9.8	4.2	7410	0.70820
Co-204	53.3	89-07-27	22.0	10000	7.0	434	240	62	3.8	1700	17	2700	< 1.0	36	8.4	3.4	5400	0.70820
Co-205	25.9	89-07-27	21.0	860	7.3	483	91	28	0.68	44	4.6	17	21	35	0.51	0.1	439	- -
Co-206	- -	89-07-27	21.0	1450	7.2	829	160	50	0.72	86	6.2	59	38	37	1.3	0.2	635	- -
Co-207	- -	89-07-27	21.0	1800	7.1	856	180	54	0.93	130	7.6	120	90	36	1.9	0.2	760	- -
Co-208	- -	89-07-27	20.5	2000	7.2	905	200	66	0.94	120	7.9	130	- -	37	1.7	0.4	865	- -

Table 2.2 Chemical analyses of brines and saline waters from oil wells in Concordia, Catahoula, and Tensas Parishes.

State ID Number	Well Name	Depth in m below sea level	Sample Date (YY-MM-DD)	Specific Conductance (mS/cm @ 25°C)	Alkalinity (mg/L HCO3)	Ca (mg/L)	Mg (mg/L)	Ba (mg/L)	Na (g/L)	K (mg/L)	Cl (g/L)	SO4 (mg/L)	SiO2 (mg/L)	Sr (mg/L)	Br (mg/L)	Dissolved Solids (g/L)	87Sr/86Sr	δ18O ‰	δD ‰
80417	McMillin 1	1317	89-02-16	130	239	1400	- -	110	37	120	67	< 1.0	18	250	64	111	0.70772	-0.85	-15.0
88238	Gillis A1	1370	89-02-15	140	234	1400	500	140	40	160	72	6.2	19	200	67	117	0.70767	-1.00	-14.5
95680	Gillis 2	1360	89-02-14	140	234	1800	450	- -	54	260	93	92	27	170	88	150	0.70772	-0.84	-14.0
95872	Gillis 3	1375	89-02-15	135	244	1400	- -	110	40	150	72	5.6	17	170	67	116	0.70788	-0.85	-15.0
98906	Gillis B1	1373	89-02-15	140	244	1400	490	140	39	110	- -	8.3	18	200	66	116	0.70769	-0.85	-14.0
105062	Calvert 3	1557	89-01-26	190	249	1300	460	210	42	220	76	17	19	200	70	126	0.70763	-1.00	-13.0
107536	Calvert 6	1536	89-01-26	150	268	1600	470	200	47	190	77	< 1.0	19	190	65	129	0.70772	-1.40	-13.0
119940	Rhodes B1	1187	89-04-25	160	234	1100	460	150	37	160	65	< 1.0	20	190	66	107	0.70728	-1.20	-12.5
120339	Testa 6	1187	89-04-25	150	258	1100	460	160	35	150	61	< 1.0	20	200	67	105	0.70725	-1.20	-13.0
121879	Rhodes C1	1079	89-04-24	130	400	840	550	84	31	120	65	< 1.0	20	180	56	90.5	0.70728	- -	- -
124885	Rhodes C2	1116	89-04-25	125	619	800	560	100	29	140	51	< 1.0	19	170	57	82.6	0.70732	-1.40	-13.0
127547	Testa D2	1342	89-04-25	145	249	1100	460	140	38	140	63	< 1.0	21	190	61	105	0.70726	-1.05	-15.5
158070	Rhodes D1	1373	89-04-24	160	244	1300	470	240	43	180	71	< 1.0	22	200	70	120	0.70749	-1.05	-14.0
165026	Quinn B1	1986	89-02-13	160	- -	1400	510	140	41	160	71	3.5	19	210	66	115	0.70805	-0.70	-12.5
182150	Quinn A1	2028	89-04-28	165	- -	1500	420	- -	50	270	86	43	22	150	- -	147	0.70797	-0.70	-14.0
204281	White et al. 2	1795	89-04-27	210	234	1400	410	270	52	260	90	< 1.0	20	150	87	148	0.70807	-1.05	-14.0
205722	Pinhook 8	1803	89-04-27	195	244	1400	390	310	53	280	88	< 1.0	20	150	81	147	0.70797	-1.00	-14.0
208729	Lawrence 3	1796	89-04-27	170	244	1400	400	290	57	250	87	< 1.0	20	150	86	138	0.70800	-0.95	-15.0

BRACKISH WATER

Areal Distribution of Brackish Water

Concentrations of dissolved solids reach maximum values in the Alluvial Aquifer and the uppermost part of the Jasper aquifer system near the location of plugged and abandoned oil wells and test holes (fig. 2.4). The proximity of maximum concentrations of dissolved solids suggests that these oil wells and test holes may provide avenues for upward migration of saline waters or brines from depth.

Vertical Distribution of Brackish Water

Salinity of ground water in the study area generally increases with depth. Winslow and others (1968) reported the occurrence of ground water in the study area with a dissolved-solids concentration of 1,000 mg/L at approximately 150 m (500 ft) below sea level; a dissolved-solids concentration of 3,000 mg/L at approximately 200 m (650 ft) below sea level; and a dissolved-solids concentration of 10,000 mg/L at approximately 300 m (1,000 ft) below sea level. The general pattern of increasing ground-water salinity with depth reported by Winslow and others (1968) was supported by chemical analysis of a ground-water sample from well Co-43. Well Co-43 is screened

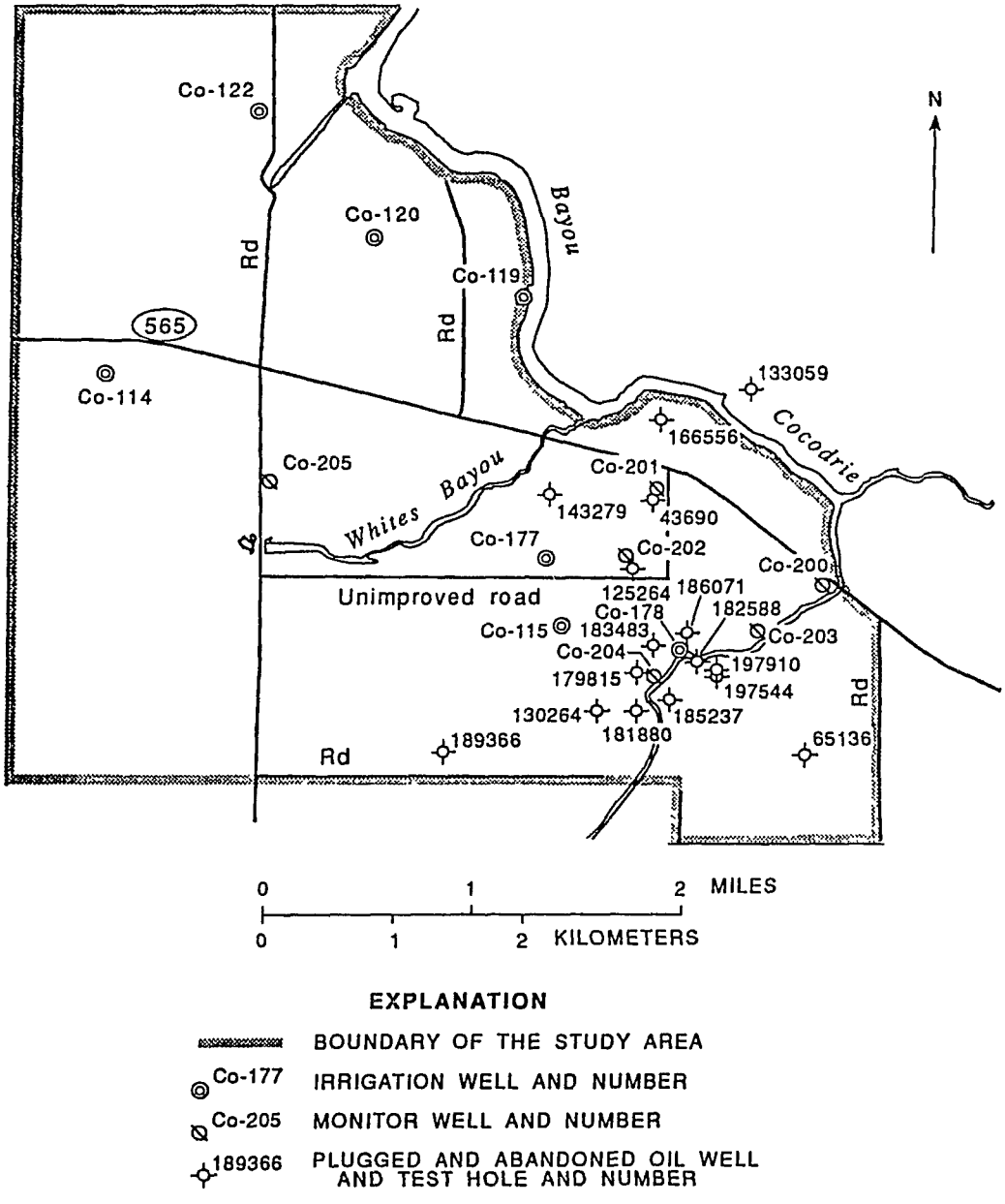


Figure 2.4 Concentrations of dissolved solids in irrigation and monitor wells.

at 195 m (640 ft) below sea level and yielded ground water with a dissolved-solids concentration of 1,490 mg/L in 1967.

Ground-water salinity within the study area apparently increases rapidly with depth within the Alluvial Aquifer and the uppermost part of the Jasper aquifer system. This apparent rapid increase of dissolved solids concentrations with depth likely results from the proximity of monitor wells to the known locations of plugged and abandoned oil wells and test holes and the presence of both fresh and brackish water over the screened intervals of irrigation rather than a general areal increase of salinity with depth.

The cause of elevated concentrations of dissolved solids in wells Co-119 and Co-200 is not well understood. One possible source of contamination in these wells is additional unlocated abandoned oil well(s). Also, density-driven flow of saline water from the area of known oil wells and test holes along a northward or northeastward sloping localized clay interval in the Alluvial Aquifer could account of increased concentrations of dissolved solids in wells Co-119 and Co-200.

Composition of Fresh and Brackish Water

A plot of Cl versus Br in water from the Alluvial Aquifer and the uppermost part of the Jasper aquifer system and saline waters and brines from the Wilcox aquifer show a strong linear trend (r=0.99 based on linear least-squares

regression) (figs. 2.5 and 2.6). The best agreement between data and the best-fit line occurs for Cl concentrations which equal or exceed approximately 500 mg/L. Analytical uncertainty in determining low concentrations of Br or sources of Br additional to those which participate in the formation of brackish water may contribute to the lack of agreement in water having Cl concentrations less than approximately 500 mg/L. The linear relationship shown in figures 2.5 and 2.6 indicates that brackish water in the Alluvial Aquifer and the uppermost part of the Jasper aquifer system could be derived from mixing of freshwater from the Alluvial Aquifer or from the uppermost part of the Jasper aquifer system with saline waters or brines from the Wilcox aquifer.

Values of $^{87}Sr/^{86}Sr$ in brackish water from the uppermost part of the Jasper aquifer system taken from wells Co-200, Co-201, Co-202, Co-203, and Co-204 and saline waters and brines from the Wilcox aquifer are plotted against 1/Sr in figure 2.7. Values of $^{87}Sr/^{86}Sr$ plotted against 1/Sr follow a linear relation (r=0.94 based on linear least-squares regression).

The concentration of Sr in saline waters and brines and from the Wilcox aquifer in the entire Concordia Parish study area ranges from 150 mg/L to 250 mg/L. The corresponding values of 1/Sr are 0.0067 L/mg and 0.0040 L/mg respectively. Extrapolation of the best-fit line in figure 2.7 to a value of 0.0040 L/mg for 1/Sr yields an $^{87}Sr/^{86}Sr$ value of

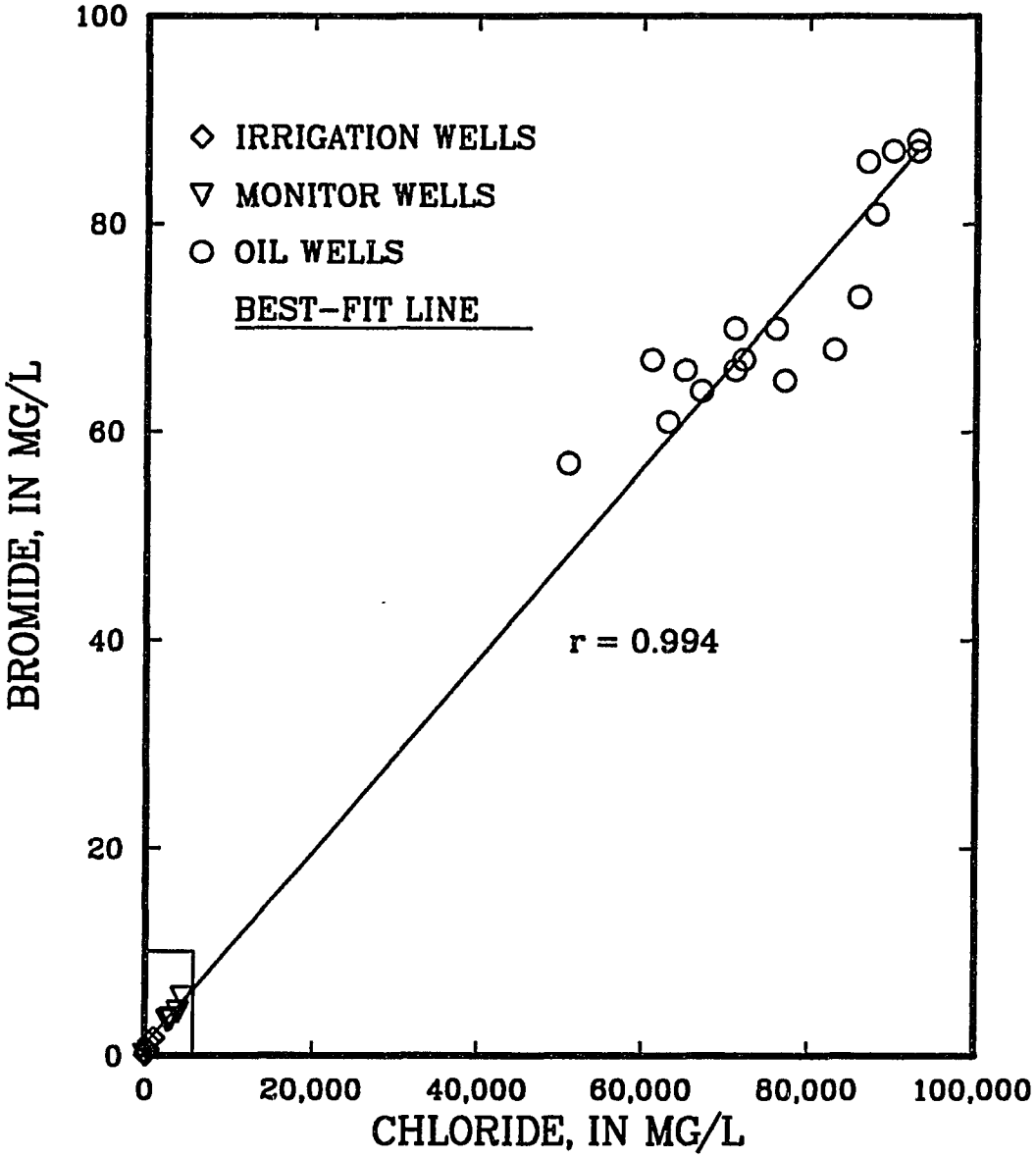


Figure 2.5 Br concentration as a function of Cl concentration in irrigation, monitor, and oil wells.

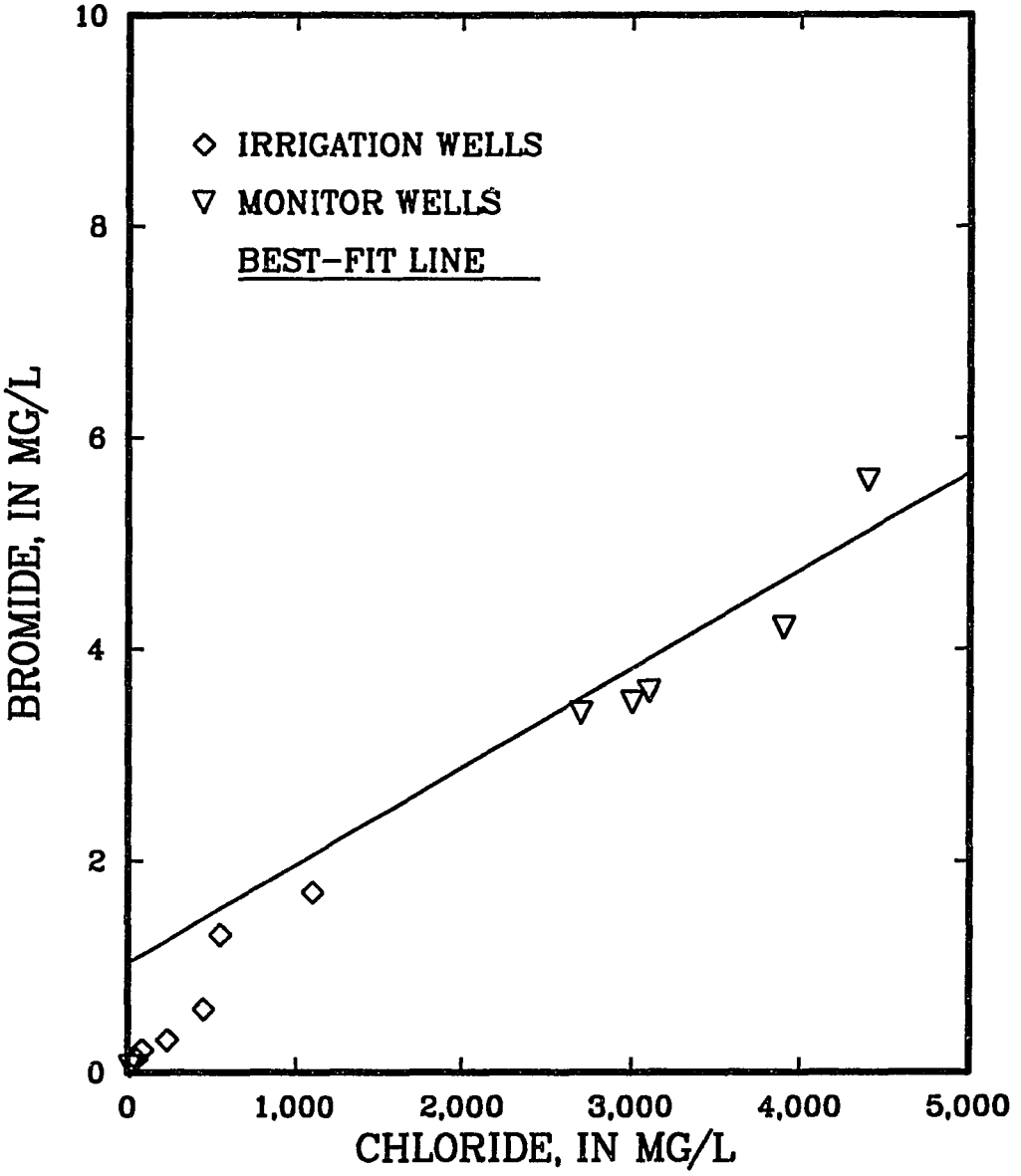


Figure 2.6 Enlargement of boxed area in figure 2.5.

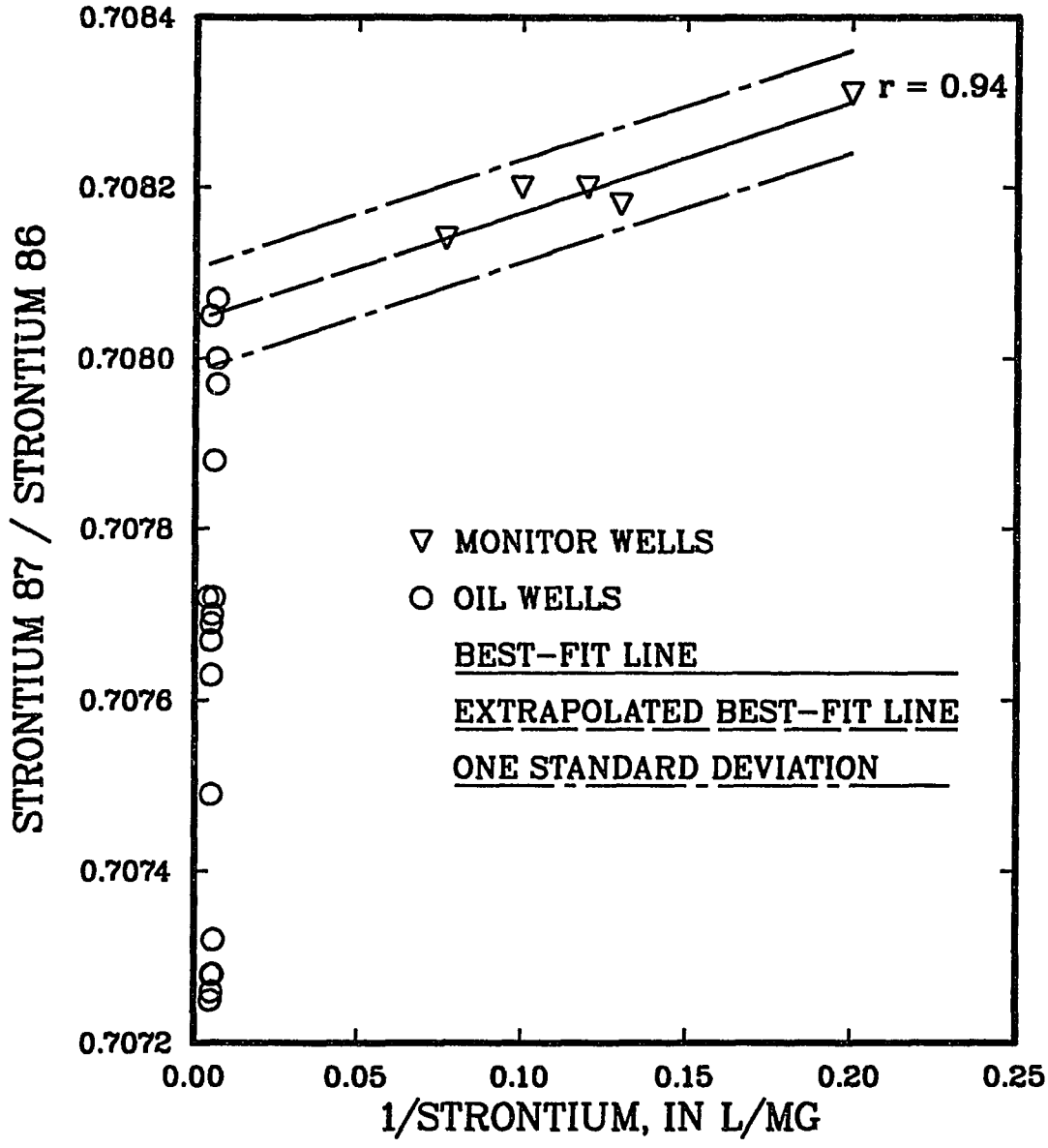


Figure 2.7 $^{87}Sr/^{86}Sr$ as a function of 1/Sr in monitor and oil wells.

0.70805. The standard deviation of $^{87}Sr/^{86}Sr$ values in brackish water from the uppermost part of the Jasper aquifer system is 0.00006. The standard deviation alone has no statistical significance in describing how well 1/Sr predicts values of the $^{87}Sr/^{86}Sr$ ratio. Rather, the standard deviation is used as a systematic approach to bracket values predicted using the best-fit line.

The lines parallel to the best-fit line in figure 2.7 graphically represent the value of one standard deviation of values of $^{87}Sr/^{86}Sr$ on either side of the best-fit line. All points representing samples from the uppermost part of the Jasper aquifer system fall within one standard deviation on either side of the best-fit line.

Extrapolation of the lines representing one standard deviation to a 1/Sr value of 0.0040 L/mg yields an intercept value of 0.70805 ± 0.00006. This intercept value represents the range of $^{87}Sr/^{86}Sr$ values in the high-strontium end member which is mixing with freshwater from the uppermost part of the Jasper aquifer system to form brackish water.

Origin of Brackish Water

Monitor well Co-202 yielded water from the uppermost part of the Jasper aquifer system having a dissolved-solids concentration of 8,410 mg/L. Ground water with a dissolved-solids concentration of 8,410 mg/L should first occur between approximately 200 and 245 m (650 and 800 ft) below

sea level corresponding to an elevation near the base of the Jasper aquifer system. Thus, it is reasonable to assume that brackish water in well Co-202, and in the Alluvial Aquifer and the uppermost part of the Jasper aquifer system originated at depths greater than or equal to 200 to 245 m (650 to 800 ft) below sea level in the Catahoula, Cockfield, Sparta, or Wilcox aquifers.

As shown in figure 2.5, the relation between Br and Cl in ground water from irrigation and monitor wells having Cl concentrations of greater than approximately 500 mg/L is consistent with mixing of freshwater from the Alluvial Aquifer or the uppermost part of the Jasper aquifer system with saline waters or brines from the Wilcox aquifer. Hanor (1984; 1987, p. 81-82) and Bennett and Hanor (1987) have proposed that saline waters and brines within Tertiary aquifers in south Louisiana were created by subsurface dissolution of halite from salt domes. If saline waters and brines in Tertiary aquifers of south central Louisiana have also originated form dissolution of halite then it is likely that the geochemistry of Br and Cl would show a great deal of interaquifer similarity. As such, any relation between Br and Cl alone is insufficient to identify sources of salinity in the Alluvial Aquifer or the uppermost part of the Jasper aquifer system.

The $^{87}Sr/^{86}Sr$ value of saline waters and brines from the Wilcox aquifer systematically increases with depth (fig. 2.8). The range of $^{87}Sr/^{86}Sr$ values in the high-strontium

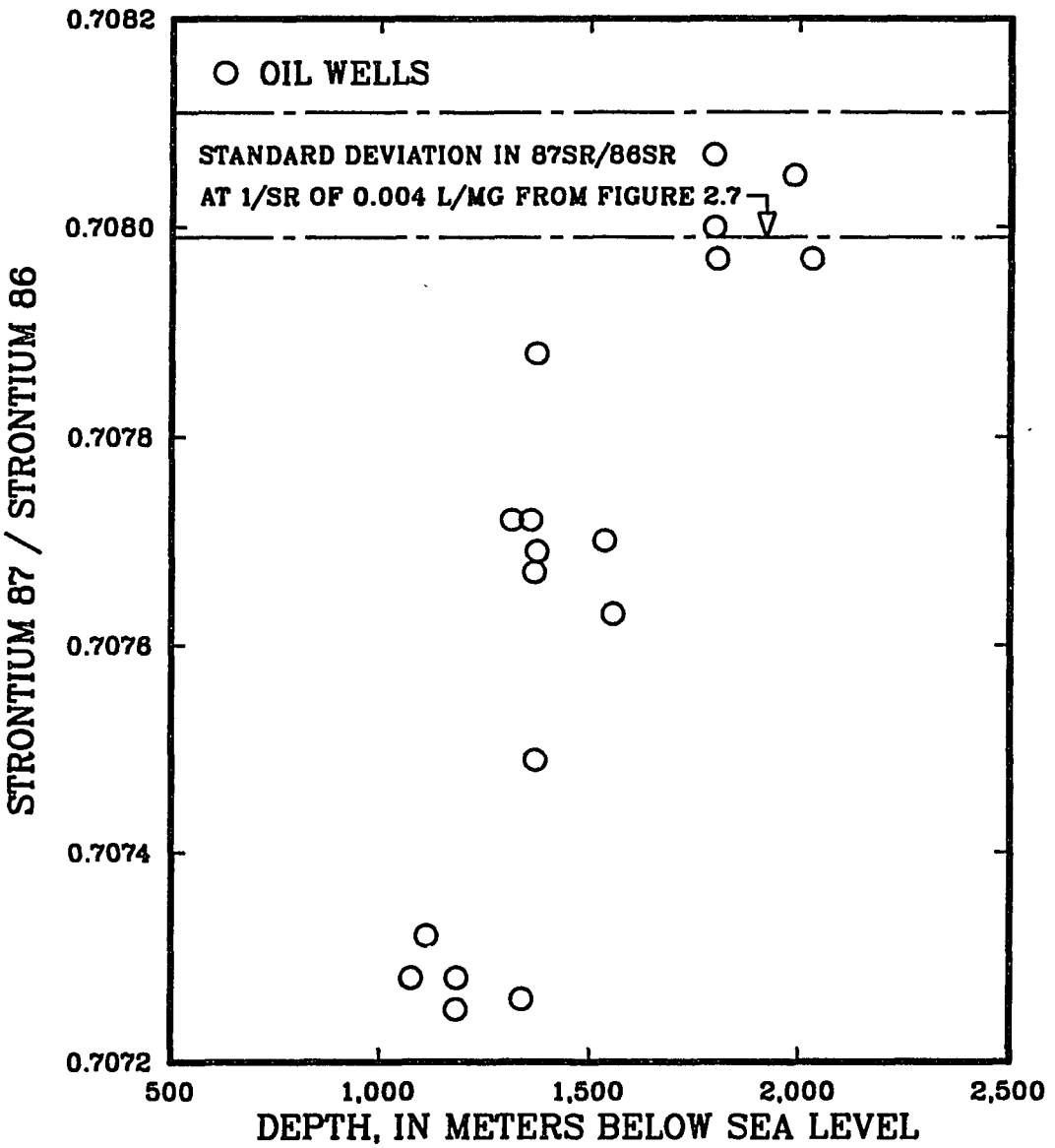


Figure 2.8 $^{87}Sr/^{86}Sr$ as a function of depth in oil wells.

end member, as defined in figure 2.7, coincide with the $^{87}Sr/^{86}Sr$ ratios in saline waters and brines from the Wilcox aquifer at 1750 to 2100 m (5,800 to 6,800 ft) below sea level (fig. 2.7).

VERTICAL MOVEMENT OF BRINES AND SALINE WATERS

Of the 16 plugged and abandoned oil wells and test holes shown in figure 2.3, 11 reached depths between 1,750 and 2,100 m (5,800 and 6,800 ft) below sea level. Given the spatial association of maximum concentrations of dissolved solids in the Alluvial Aquifer and the uppermost part of the Jasper aquifer system with the location of plugged and abandoned oil wells and test holes, it is likely that these abandoned oil wells and test holes provide an avenue for upward movement of saline waters and brines from the Wilcox aquifer. The geochemistry of Br, Cl, and Sr in waters from the Alluvial Aquifer, the uppermost part of the Jasper aquifer system, and the Wilcox aquifer also support this conclusion. The numerical simulation of Williamson and others (1990) indicated a predevelopment freshwater-equivalent head of approximately 69 m (220 ft) above land surface in the Wilcox aquifer in the study area. Because of the small withdrawl of water from the Wilcox aquifer in eastern central Louisiana, the predevelopment head calculated by Williamson and others (1990) accurately reflect present-day conditions. This head represents the

potential required to bring Wilcox brines to or near land surface in the study area.

CHAPTER SUMMARY

Samples of water from irrigation and monitor wells screened within the Alluvial Aquifer and the uppermost part of the Jasper aquifer system show the presence of brackish water in proximity to plugged and abandoned oil wells and test holes. Brackish water in the Alluvial Aquifer and uppermost part of the Jasper aquifer system is interpreted to be a mixture of fresh water and saline waters or brines from depth. Saline waters and brines from the Wilcox aquifer at depths of 1,750 to 2,100 m (5,800 to 6,800 ft) below sea level have Br and Cl geochemistry and $^{87}Sr/^{86}Sr$ values consistent with those required to generate brackish water in the Alluvial Aquifer and the uppermost part of the Jasper aquifer system by mixing with fresh ground water. Plugged and abandoned oil wells and test holes which penetrate to depths of 1,750 to 2,100 m (5,800 to 6,800 ft) below sea level provide avenues of movement for saline waters and brines in the Wilcox aquifer into the Alluvial Aquifer and the uppermost part of the Jasper aquifer system.

CHAPTER III

BRINES AND SALINE WATERS FROM THE UPPER AND MIDDLE UNITS OF THE WILCOX AQUIFER IN EASTERN CENTRAL LOUISIANA

PURPOSE

Elemental and isotopic signatures were used in Chapter II to trace the origin of brackish water in the Alluvial Aquifer of south central Concordia Parish to contamination by brines and saline water in the Wilcox aquifer. In order to confidently apply these signatures to solute source tracing the hydrogeologic controls on the abundance of Br, Cl, and the ratios of Sr isotopes in the Wilcox aquifer should be understood.

The geochemistry of Br, Cl, and the isotopes of Sr, H and O in subsurface brines and saline waters, particularly those of the Gulf Coast, have been discussed in detail in Chapter I. Briefly, the Br/Cl ratios of Gulf Coast brines and saline waters has been proposed to be controlled by dissolution of halite (Hanor, 1987; Bennett and Hanor, 1987) and recrystallization of halite (Stoessell and Moore, 1983; Morton and Land, 1987; Land and others, 1988). Br is preferentially partitioned into the aqueous phase on precipitation or recrystallization of halite. As such, precipitation or recrystallization of halite produces formation water which is enriched in Br relative to the

precipitating or recrystallizing halite. In contrast, congruent dissolution of halite produces formation water which has the same Br/Cl ratio as the dissolving halite.

Recent work by Chaudhuri and Clauer (1993) emphasized the importance of alteration and dissolution of alkali feldspars and mica and illitization of smectite in determining the $^{87}Sr/^{86}Sr$ ratio of subsurface brines and saline waters from a number of sedimentary hydrogeologic settings. Land and Macpherson (1992) have suggested dissolution of plagioclase and skeletal marine carbonates as important sources of Sr in formation waters in Cenozoic sediments of the Gulf Coast. In addition, strontianite, celestite, and anhydrite present in salt domes and diapirs and salt-dome caprock may be important sources of Sr in formation waters. Posey and others (1985) have identified water-rock interaction to be a major control on the isotopic composition of O in brines and saline waters of Tertiary age in southern Louisiana.

While many eloquent geochemical arguments have been advanced concerning the sources of solutes in brines and saline waters of the Gulf Coast relatively little has been done on interpretation of the distribution of solutes in the framework of regional ground-water flow. The Concordia parish study area represents a unique opportunity in this respect because the brines and saline waters present in the Wilcox aquifer of eastern central Louisiana have no major local source of salinity such as a nearby salt dome or

diapir (Beckman and Williamson, 1990). As such, the bulk of solutes now contained in water of the Wilcox aquifer of eastern central Louisiana were transported to their present location by ground-water flow. Accordingly, the purpose of this chapter is to explain the abundance and distribution of solutes in brines and saline waters of the Concordia Parish study area in eastern central Louisiana in terms of water-rock interaction and regional ground-water flow.

DESCRIPTION OF THE STUDY AREA

The area of eastern central Louisiana from which data was collected includes Concordia, and adjoining areas of Catahoula and Avoyelles Parishes, Louisiana and is referred to as the Concordia Parish study area in figure 1.1. Land surface within the study area has a mean elevation of approximately 15 m (50 ft) above sea level and little topographic relief.

LITHOLOGY AND HYDROGEOLOGY OF THE WILCOX AQUIFER

Wilcox sediments deposited in eastern central Louisiana represent fluvial, deltaic, and marine environments (Galloway, 1968; Lowry, 1987; Tye and others, 1991). As such, connate waters in these sediments would have contained maximum salinities equal to that of Paleocene/Eocene

seawater. In contrast, salinities in the Wilcox aquifer currently can exceed 100 g/L (Funayama, 1990).

According to the variable-density flow model of Williamson and others (1990), net vertical ground water flow in the Wilcox aquifer of the study area is upward from the lower through the middle and into the upper unit (figs. 1.10 and 1.11). Net lateral ground water flow in the Wilcox aquifer is generally from the southeast in the lower unit; from the south and southwest in the middle unit; and from the west and northwest in the upper unit (figs. 1.9, 1.10, and 1.11). It should be noted that the model of Williamson and others (1990) used to calculate these net flows was discritized into 259 km^2 (100 mi^2) blocks. This coarse discritization allows calculation of net flows over large areas but does not permit exact calculation of flow rates and directions within smaller areas. As a result, calculated net flow rates and directions are valid on a regional scale but local variations in flow rate and directions may exist.

DATA COLLECTED

Locations of all sampled oil wells are shown in figures 2.1 and 3.1. Results of all analyses of saline waters and brines are given in table 2.2. Bottom-hole temperatures from sampled oil wells were recorded from header information of geophysical logs. Corrected bottom-hole temperatures were derived from recorded bottom-hole temperatures using the

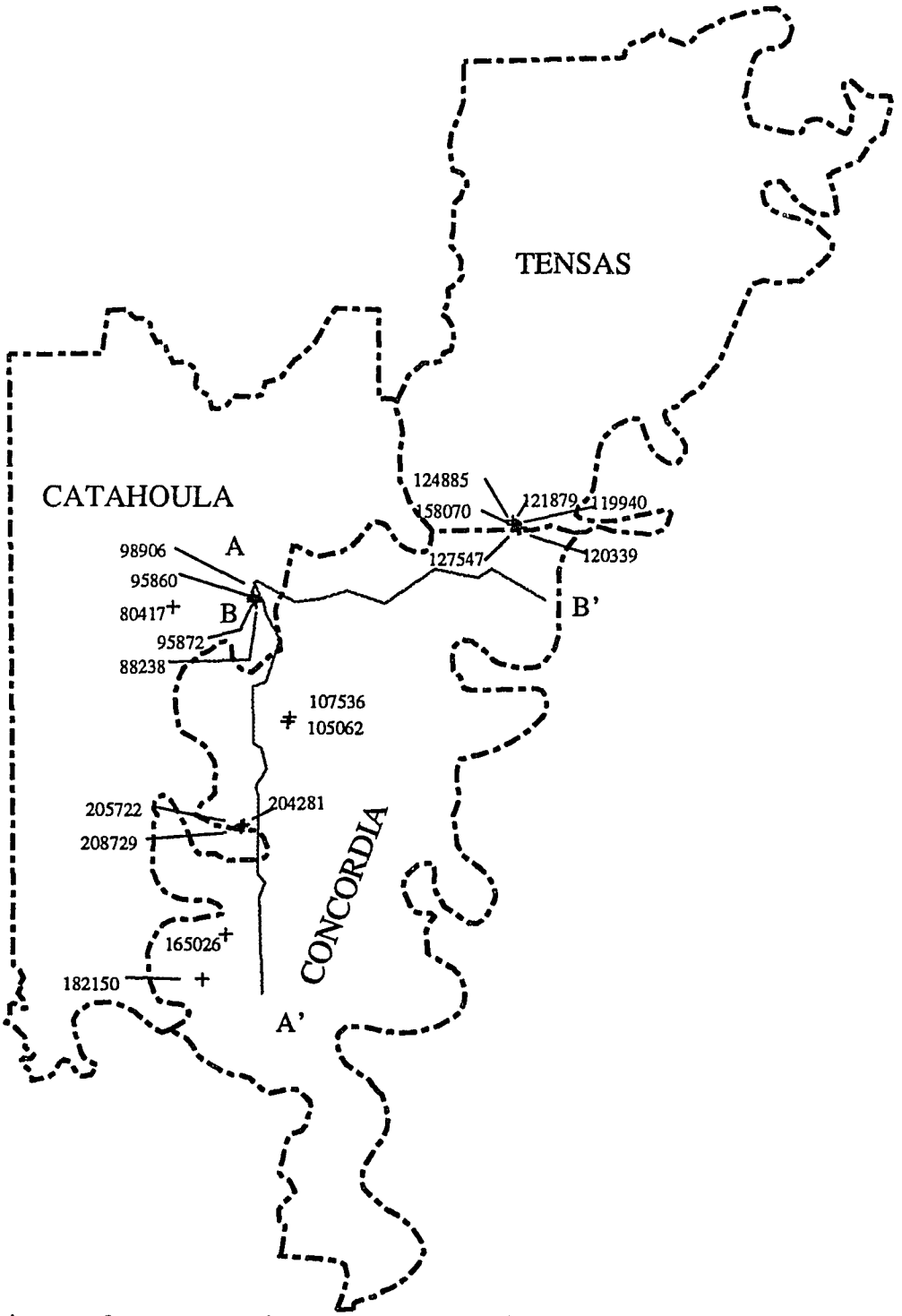


Figure 3.1 Locations and State identification numbers of sampled oil wells and the locations of cross-sections A-A' and B-B'.

relationship of Kehle (1971) as cited by Hanor (1987). A linear least-squares regression of corrected bottom hole temperatures versus depth yielded a geothermal gradient of 24°C/km (1.3°F/100ft) and a mean sealevel temperature of 29.7°C (85.4°F) in the study area (fig. 3.2).

CALIBRATION OF SP-DERIVED SALINITIES

For clarity in the following discussion, the concentration of total solutes derived from SP logs will be referred to as salinity and will be expressed in g/kg. The concentration of total solutes from analytical determination of dissolved solids will be referred to as dissolved solids and expressed in g/L. Density-corrected dissolved solids which will be expressed in g/kg.

The theory of deriving ground-water salinities from SP is discussed in detail in Appendix II. Values of subsurface temperature used in salinity calculations were established using the geothermal gradient in the study area. Salinities were compared to density-corrected dissolved solids concentrations in nine of the 18 sampled oil wells. Wells in which comparisons were made were chosen using the following criteria: (1) confident picks of both baseline and maximum SP deflection with a minimum of noise, (2) drilling fluid resistivities of less than or equal to 2.6 Ω-m at 24°C (75°F), (3) sand thickness of at least 3 m (10 ft), and (4) sand depth of no more than ± 15 m (50 ft) from the screened

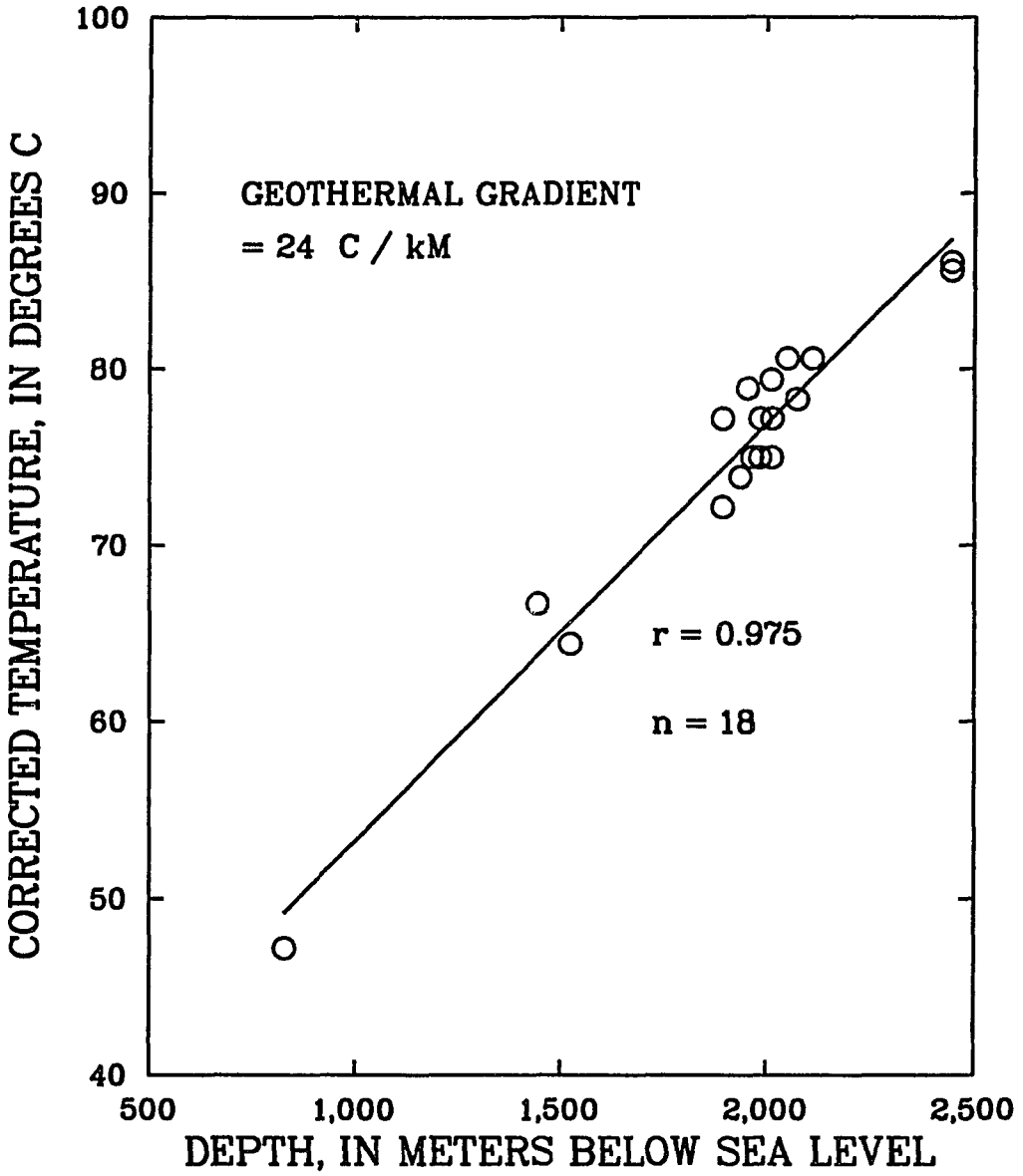


Figure 3.2 Geothermal gradient in the Concordia Parish study area.

interval of the sampled oil well. Criteria 1 through 3 were established by trial and error to give the most concordant results between SP-derived salinities and density-corrected dissolved solids concentrations based on data for all 18 sampled oil wells. Criterion 4 was established arbitrarily. Comparisons were not made in the screened intervals owing to the possible decrease in the absolute magnitude of the SSP by the hydrocarbon suppression effect (Asquith and Gibson, 1982).

Statistical results of the comparison between SP-derived salinities and density-corrected dissolved solids concentrations in the nine selected oil wells are shown in figure 3.3. Salinities are less than density-corrected dissolved solids concentrations over the entire range of values with the absolute difference in compared values decreasing with increasing salinity. Even though they differ, the two sets of values fall along a linear trend. This permitted a mathematical model based on a linear regression between the two data sets to be used to predict density-corrected dissolved solids concentration given salinity. The relationship between salinity and density-corrected dissolved solids concentration based on a linear least-squares regression model is

density-corrected dissolved solids (g/kg) =
0.663 salinity (g/kg) + 63.0 g/kg equation 3.1

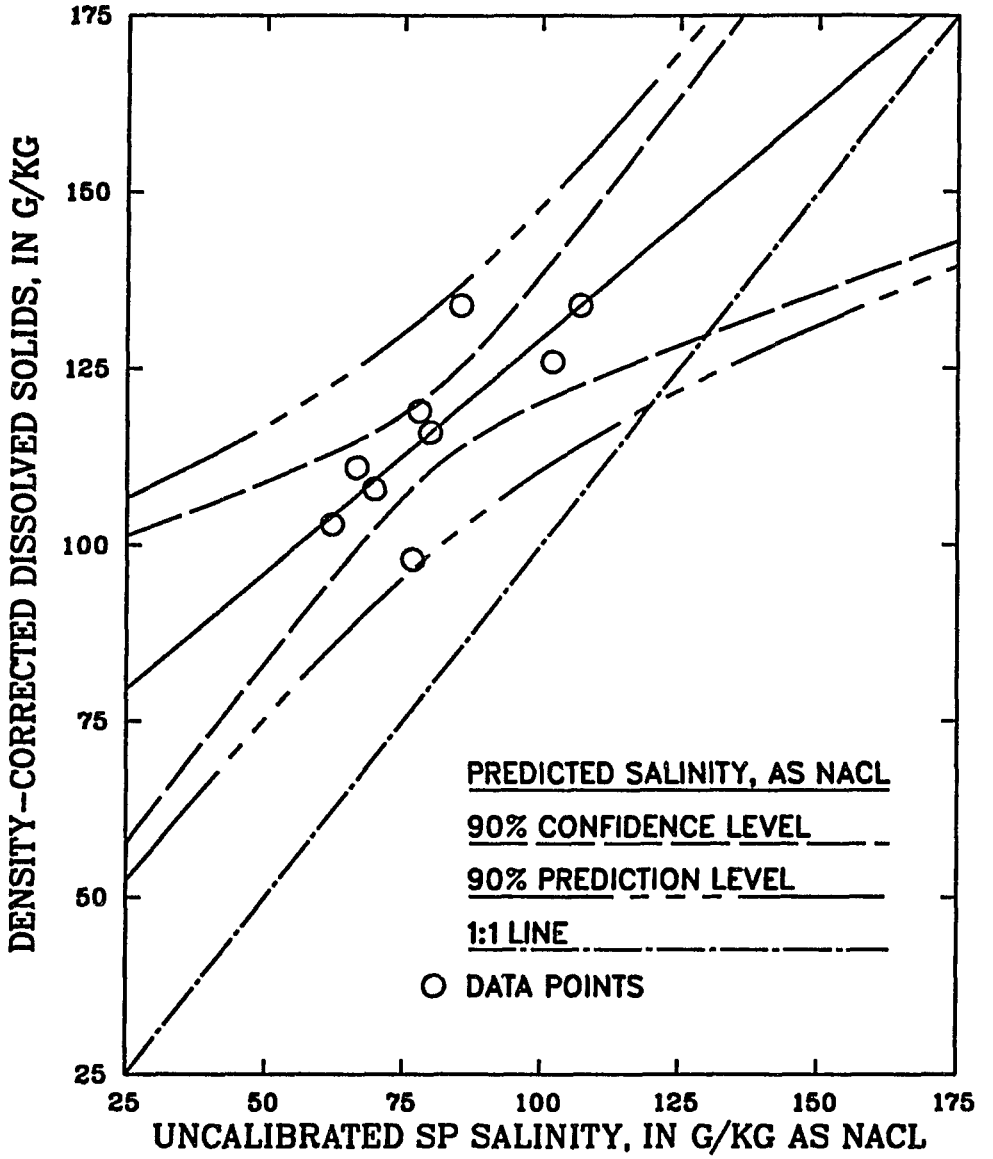


Figure 3.3 Regression line and statistical relationships between SP-derived salinity and density-corrected dissolved solids concentrations.

Figure 3.3 also shows the 90% confidence and prediction intervals associated with equation 3.1. The confidence interval brackets errors in predicting the dependent variable based on uncertainty associated with the regression model used to establish the relationship in equation 3.1. The prediction interval further accounts for the normal distribution of predicted values of the dependent variable around any value of the independent variable (Iman and Conover, 1983, p. 377-379). All density-corrected dissolved solids concentrations fall within the 90% prediction interval and seven of the nine fall within the 90% confidence interval.

LATERAL AND VERTICAL DISTRIBUTION OF SALINITY, DENSITY, AND VISCOSITY

Salinity, density, and viscosity of ground water in the upper and middle units of the Wilcox aquifer were determined along north-south (A-A') and east-west (B-B') trending cross-sections through the study area. Cross-section locations and the location of sampled oil wells are shown in figure 3.1. Logs used and intervals where SP was determined were chosen based on the four criteria previously discussed. Locations of and raw data from all SP logs used in calculating ground-water salinity, density, and viscosity along cross-sections A-A' and B-B' are listed in Appendix IV.

The salinity, density, and viscosity of Wilcox ground water as a function of depth along cross-section A-A′ is shown in figures 3.4, 3.5, and 3.6, respectively. Salinities of greater than approximately 100 g/kg occur below the Big Shale while salinities of less than or equal to approximately 100 g/kg occur above the Big Shale. Based on these limited data, salinities above the Big Shale appear to increase slightly down dip. Density shows a more complex relationship with depth reflecting the influences of both salinity and temperature. The most dense water is apparently present at the top and base of data along A-A′. The apparent presence of salinities and densities at the top of A-A′ greater than those immediately below may be artifacts of SP baseline picks in the overlying Cane River Marl. A zone of relatively low salinity is present in the southern half of A-A′ both above and below the Big Shale. The zone of low density above the Big Shale corresponds to a zone of low salinity. The low density zone below the Big Shale is smaller than the one above and may be controlled by a combination of salinity and temperature. Viscosity shows little lateral structure and increases almost monotonously with depth reflecting temperature as the primary control.

The salinity, density, and viscosity of Wilcox ground water as a function of depth along cross-section B-B′ is shown in figures 3.7, 3.8, and 3.9, respectively. Salinity shows a less regular structure along B-B′ than along A-A′. A zone of lower salinity occurs in the upper center of data

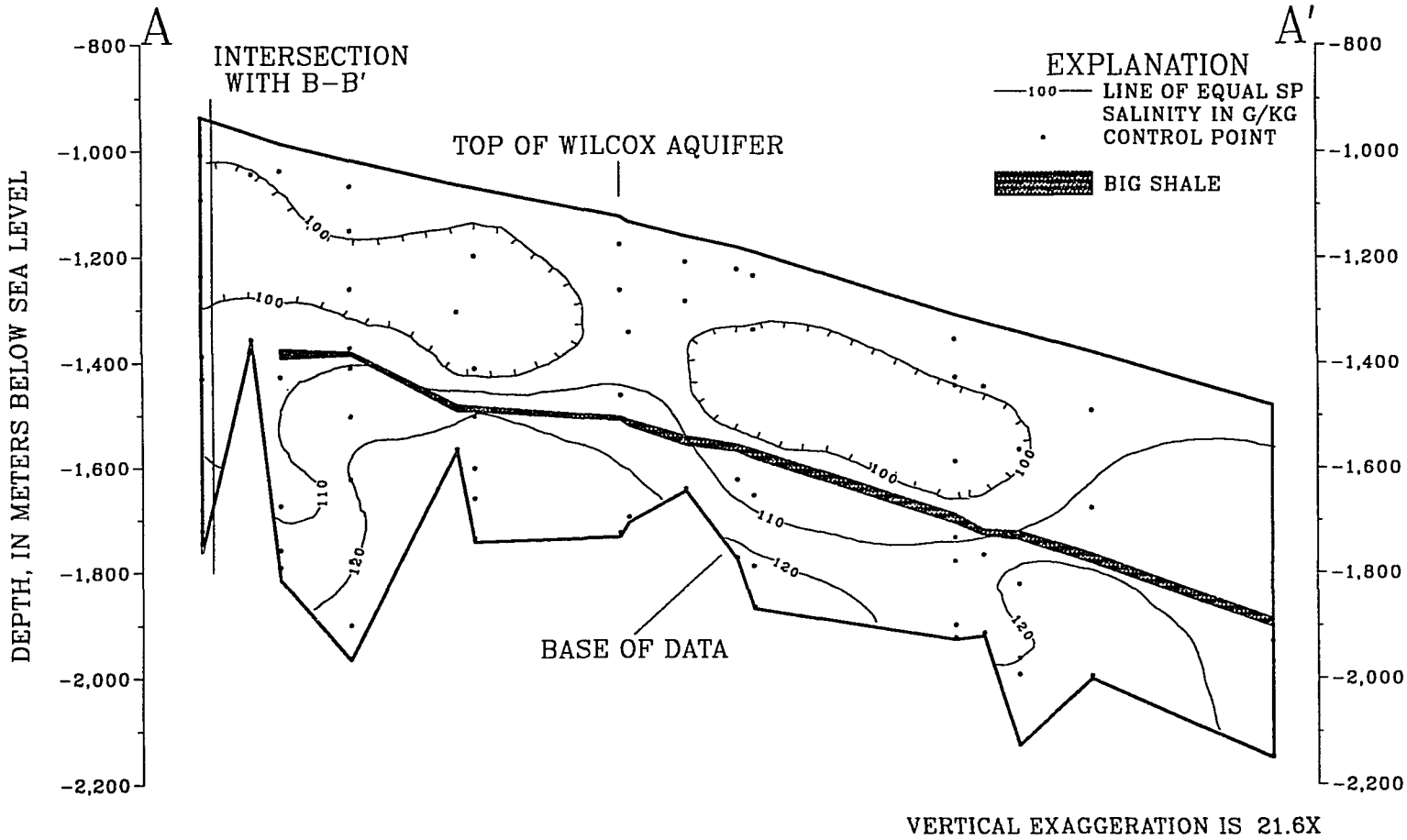


Figure 3.4 Spatial variations in salinity on cross-section A-A'.

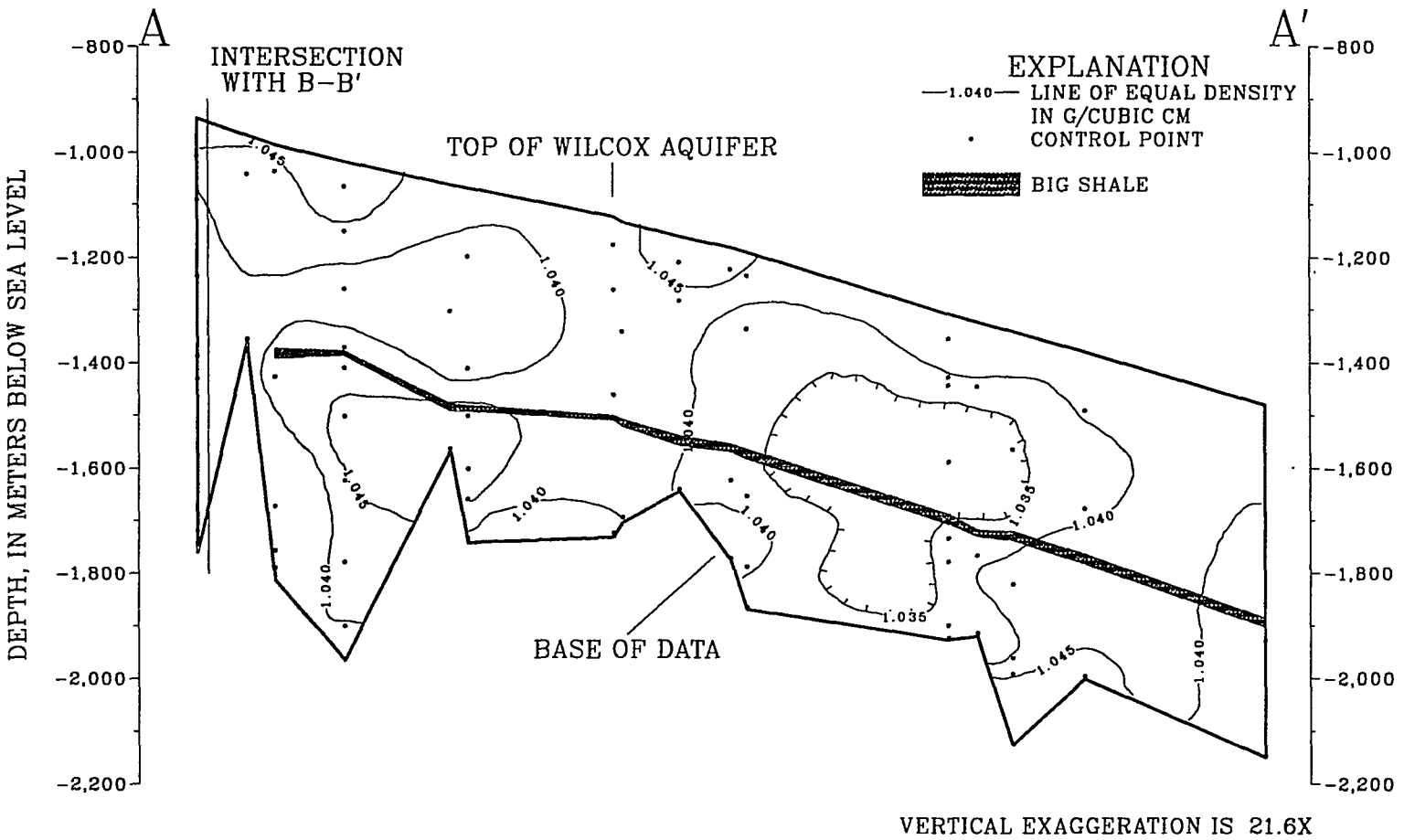


Figure 3.5 Spatial variations in in-situ fluid density on cross-section A-A'.

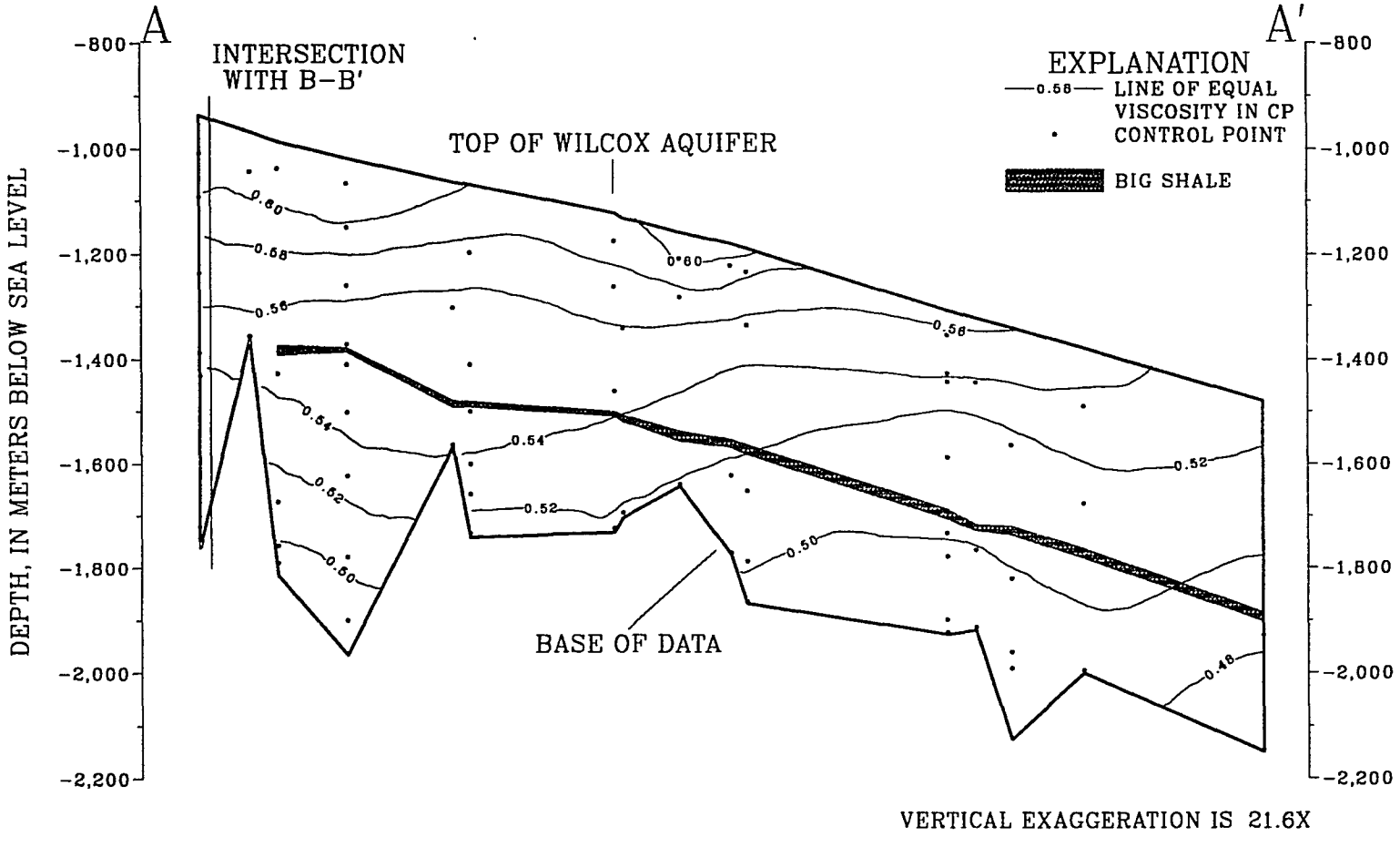


Figure 3.6 Spatial variations in in-situ fluid viscosity on cross-section A-A'.

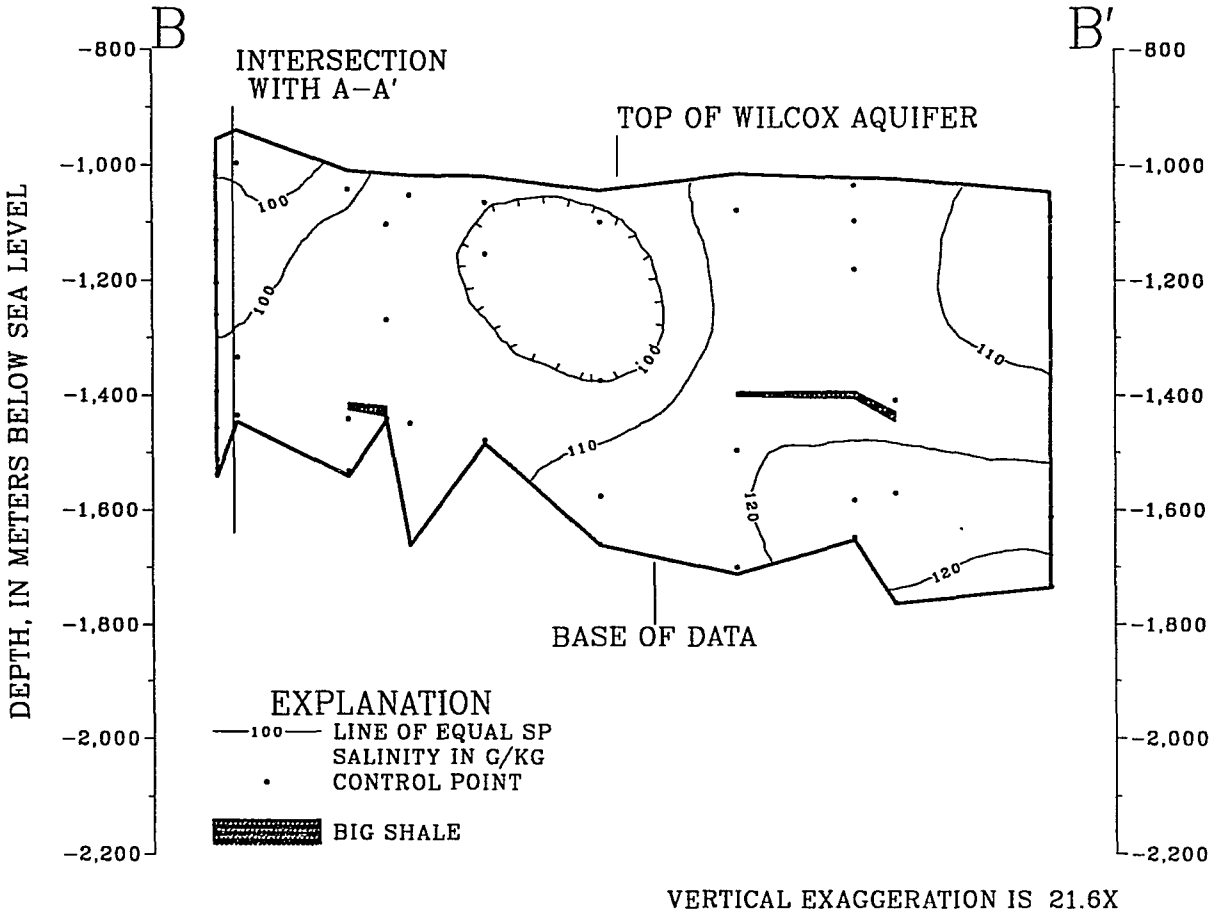


Figure 3.7 Spatial variations in salinity on cross-section B-B'.

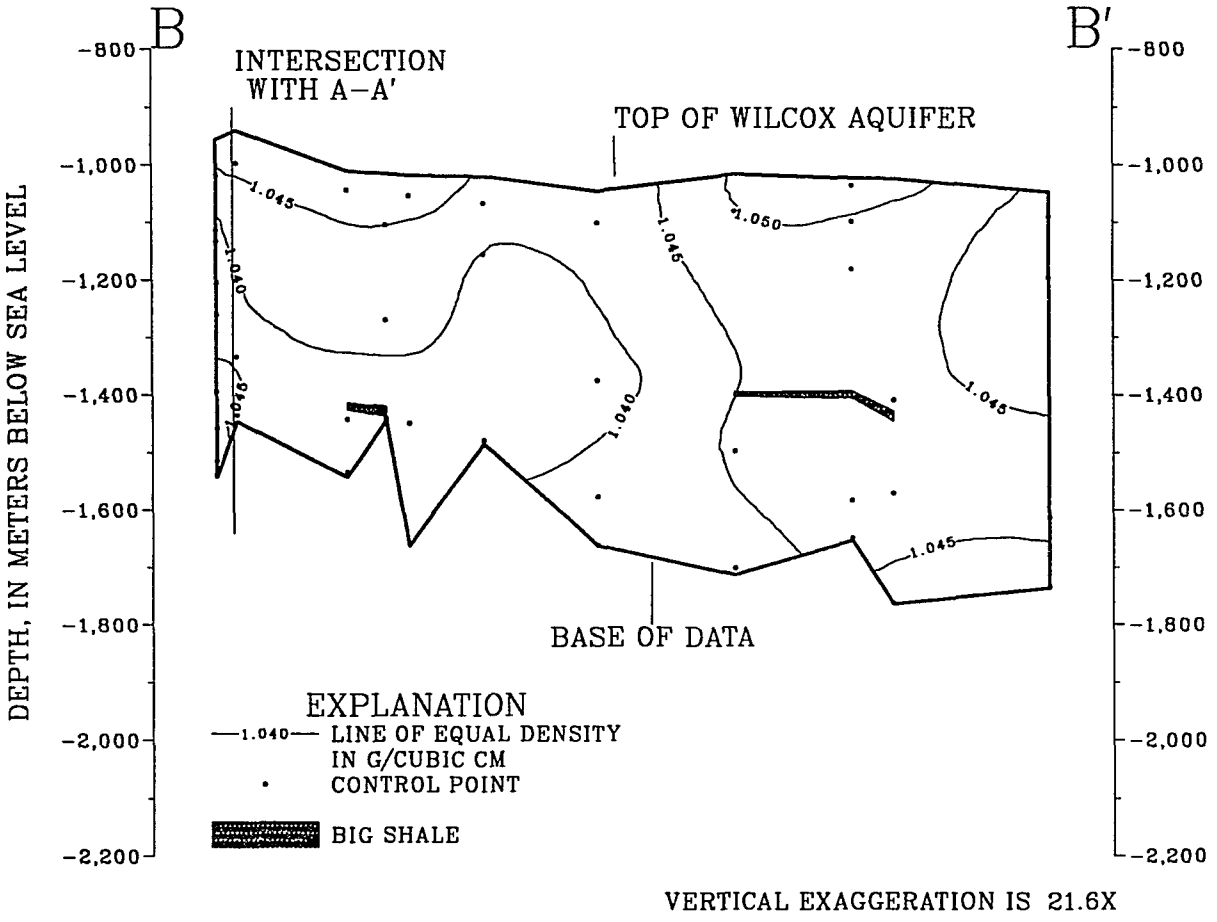


Figure 3.8 Spatial variations in in-situ fluid density on cross-section B-B'.

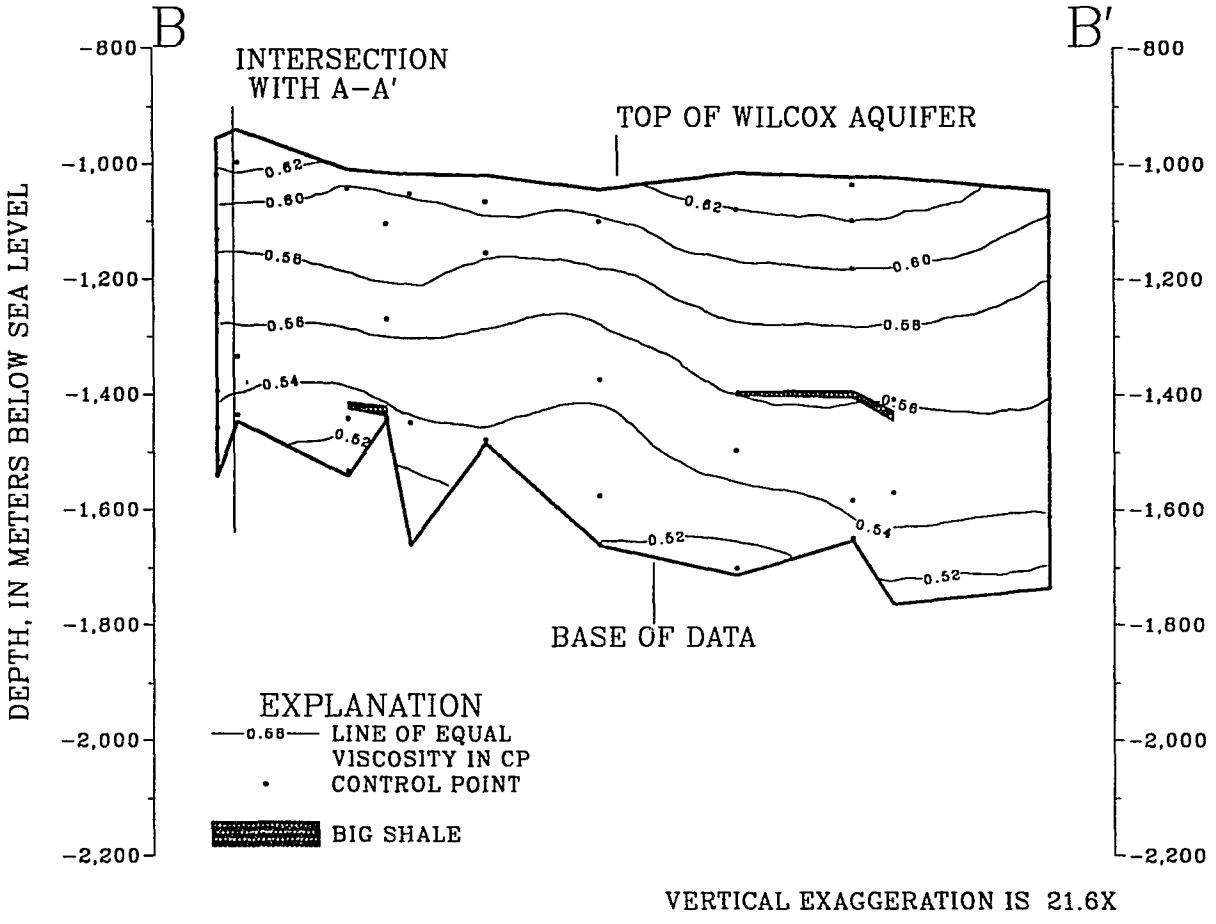


Figure 3.9 Spatial variations in in-situ fluid viscosity on cross-section B-B'.

along B-B′ and a zone of higher salinity occurs in the eastern base of data along B-B′. Density also shows less regular structure along B-B′. Viscosity, however, decreases almost monotonously with depth in a manner very similar to A-A′ again reflecting temperature as the primary control.

Oil wells which lie to the north of cross-section B-B′ are screened in the upper unit of the Wilcox aquifer with the exception of well 158070 which is screened in the middle unit of the Wilcox aquifer. All other oil wells are screened in the middle unit. Figure 3.10 shows dissolved solids concentrations in g/L as a function of depth for sampled oil wells in the upper and middle units. Wells which are screened in the upper and middle units have been identified. Generally, dissolved solids concentrations increase with depth in all sampled oil wells. However, the rate of increase with depth appears to be greater in the upper unit. Values of dissolved solids concentrations are also generally lower in wells screened in the upper unit. The apparent discrepancy in the range of values shown in figures 3.4, 3.7, and 3.10 arise from the use of density-corrected units of g/kg in the first two figures and volumetric units of g/L in the latter.

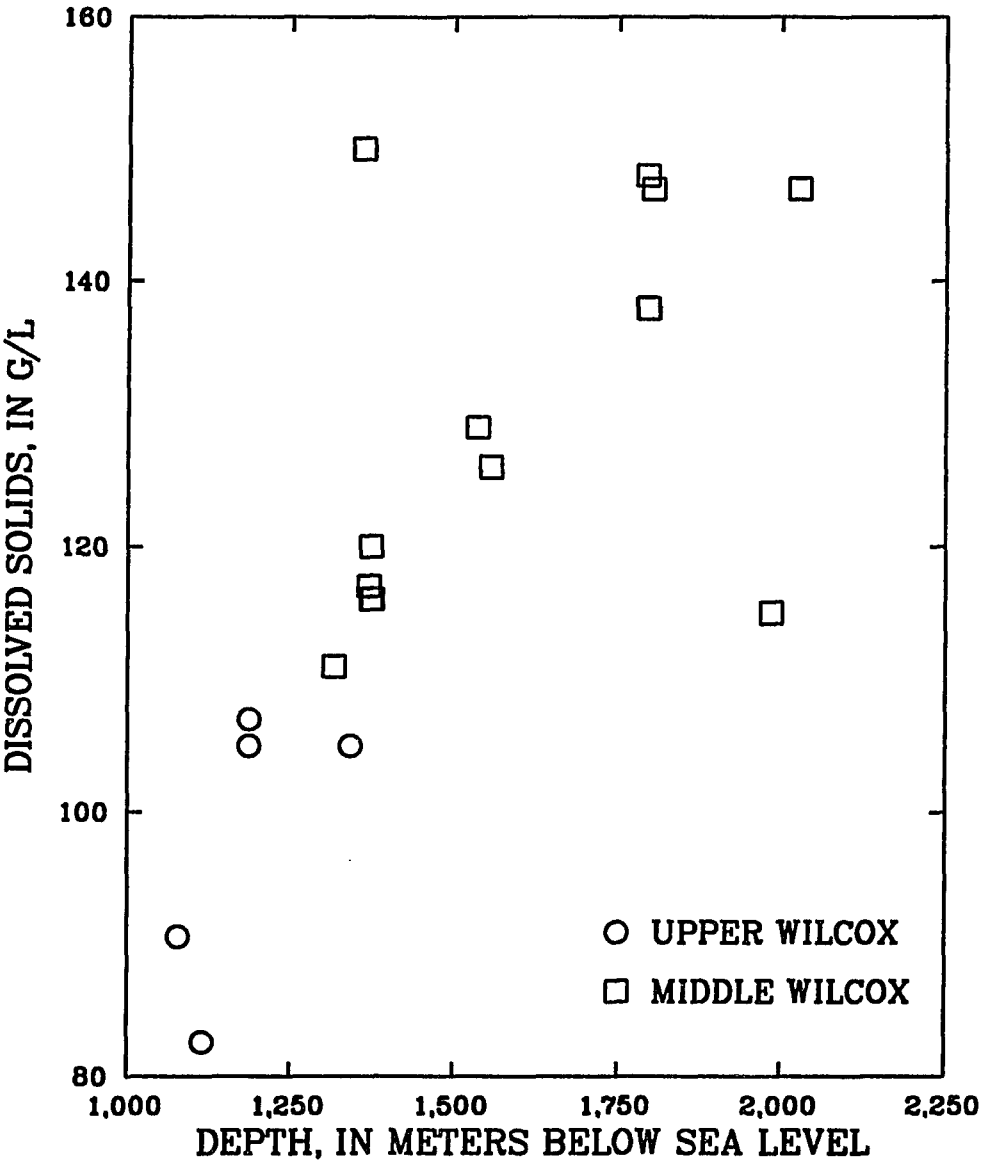


Figure 3.10 Dissolved solids concentrations as a function of depth in the upper and middle units of the Wilcox Aquifer.

COMPOSITION OF BRINES AND SALINE WATERS

Major Solutes

Concentrations of dissolved cations and anions as a function of dissolved solids are shown in figures 3.11 and 3.12, respectively. All analyzed samples are Na-Cl type waters with dissolved solids concentrations ranging from 82.6 to 150 g/L. Concentrations of dissolved Na, Ca, Ba, and K increase with increasing salinity. In contrast, concentrations of dissolved Mg decrease with increasing concentrations of dissolved solids and dissolved Sr concentrations remain virtually unchanged. Both dissolved Cl and Br concentrations increase with increasing concentrations of dissolved solids. Alkalinity displays the most complex pattern of change with increasing concentrations of dissolved solids of any major constituent. Alkalinity decreases rapidly from 600 mg/L (as HCO_3) at an dissolved solids concentration of approximately 80 g/L to less than 300 mg/L at an dissolved solids concentration of approximately 110 g/L. Alkalinity shows no systematic change with increasing salinity at dissolved solids concentrations of greater than approximately 110 g/L.

Concentrations of Br and Cl increase along a roughly linear trend for all sampled oil wells (fig. 3.13). The Br/Cl ratio shows no systematic change with increasing dissolved Cl concentration (fig. 3.14). Most Br/Cl ratios

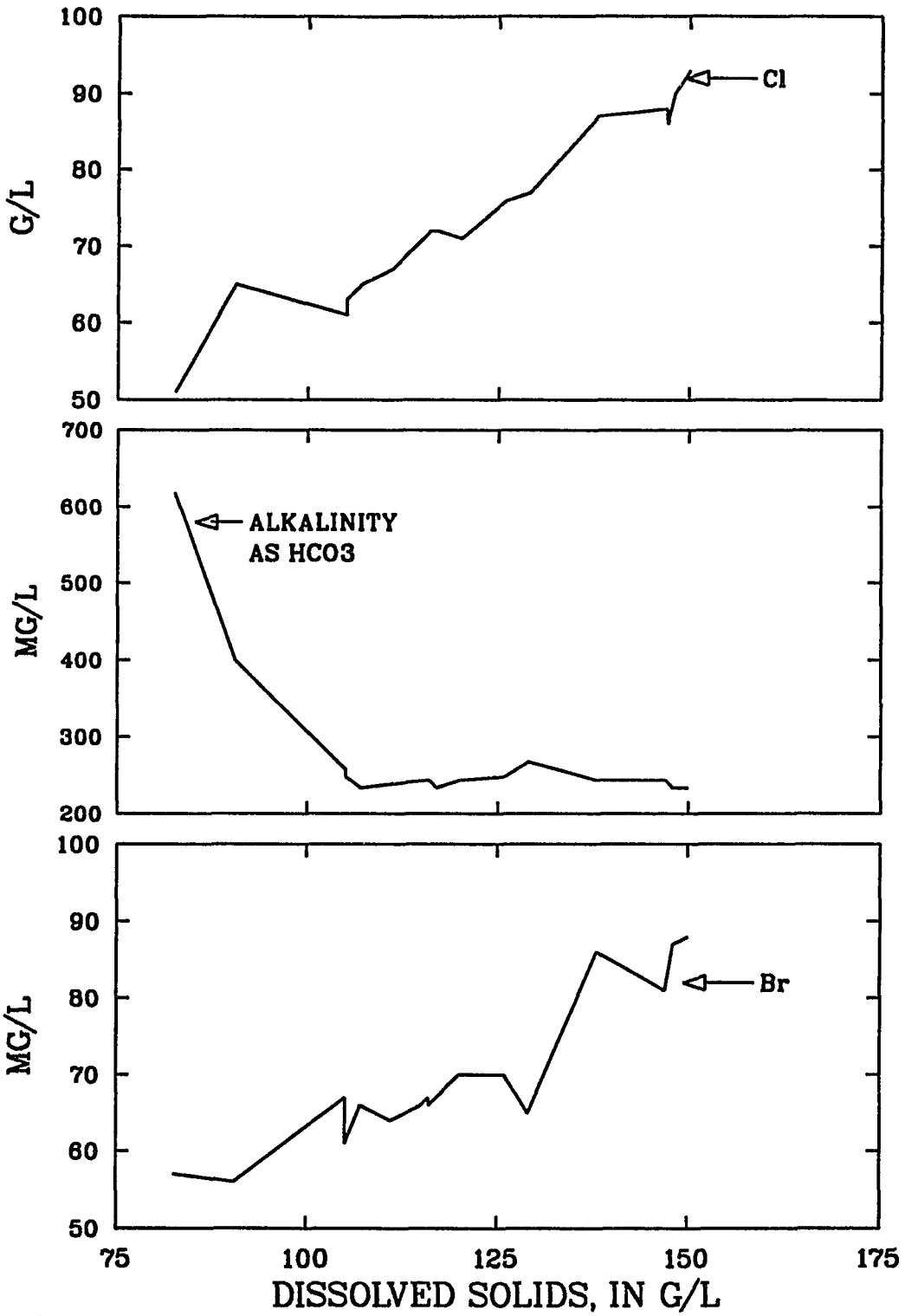


Figure 3.11 Concentrations of cations as a function of concentrations of dissolved solids.

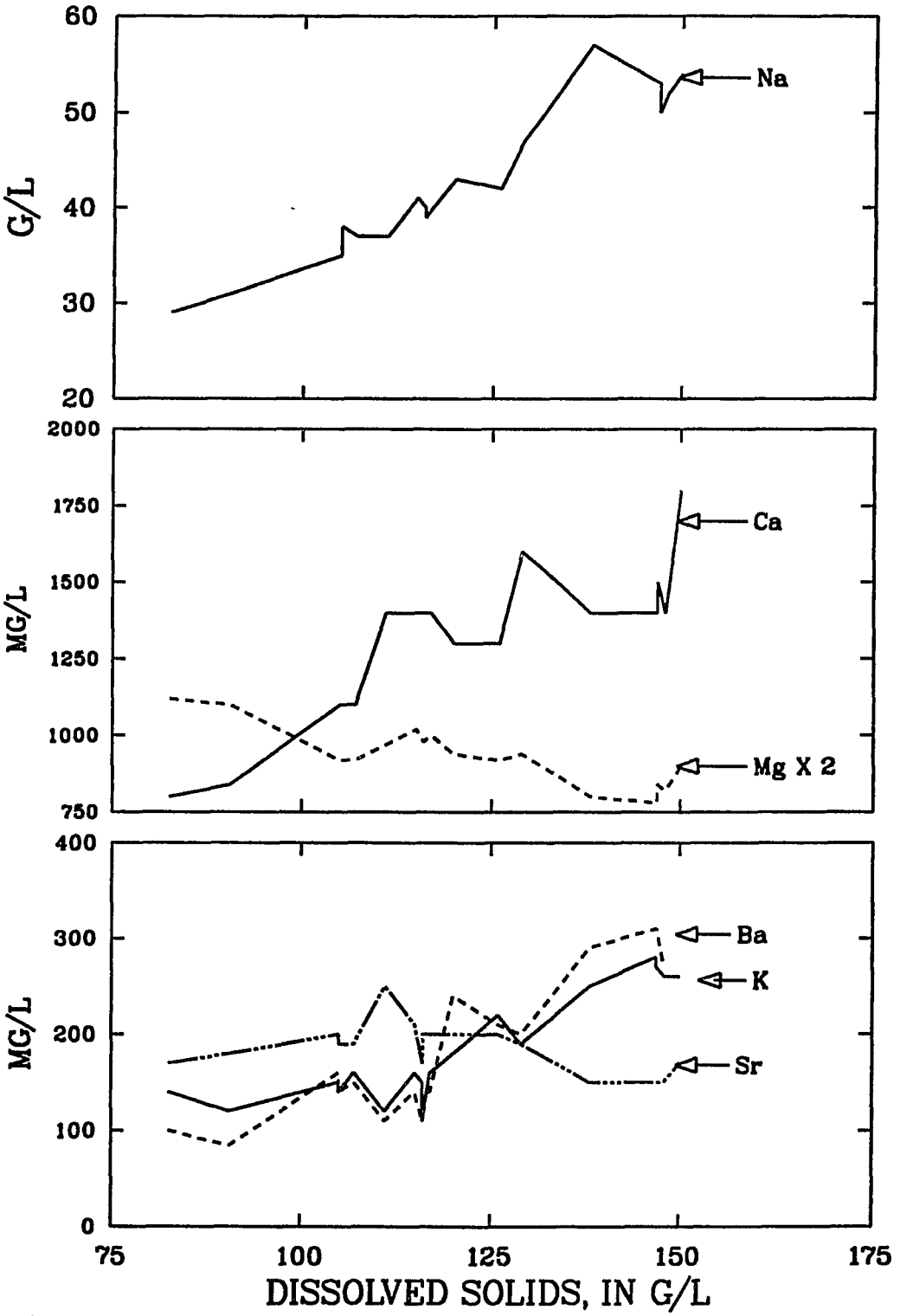


Figure 3.12 Concentrations of anions and alkalinity as a function of concentrations of dissolved solids.

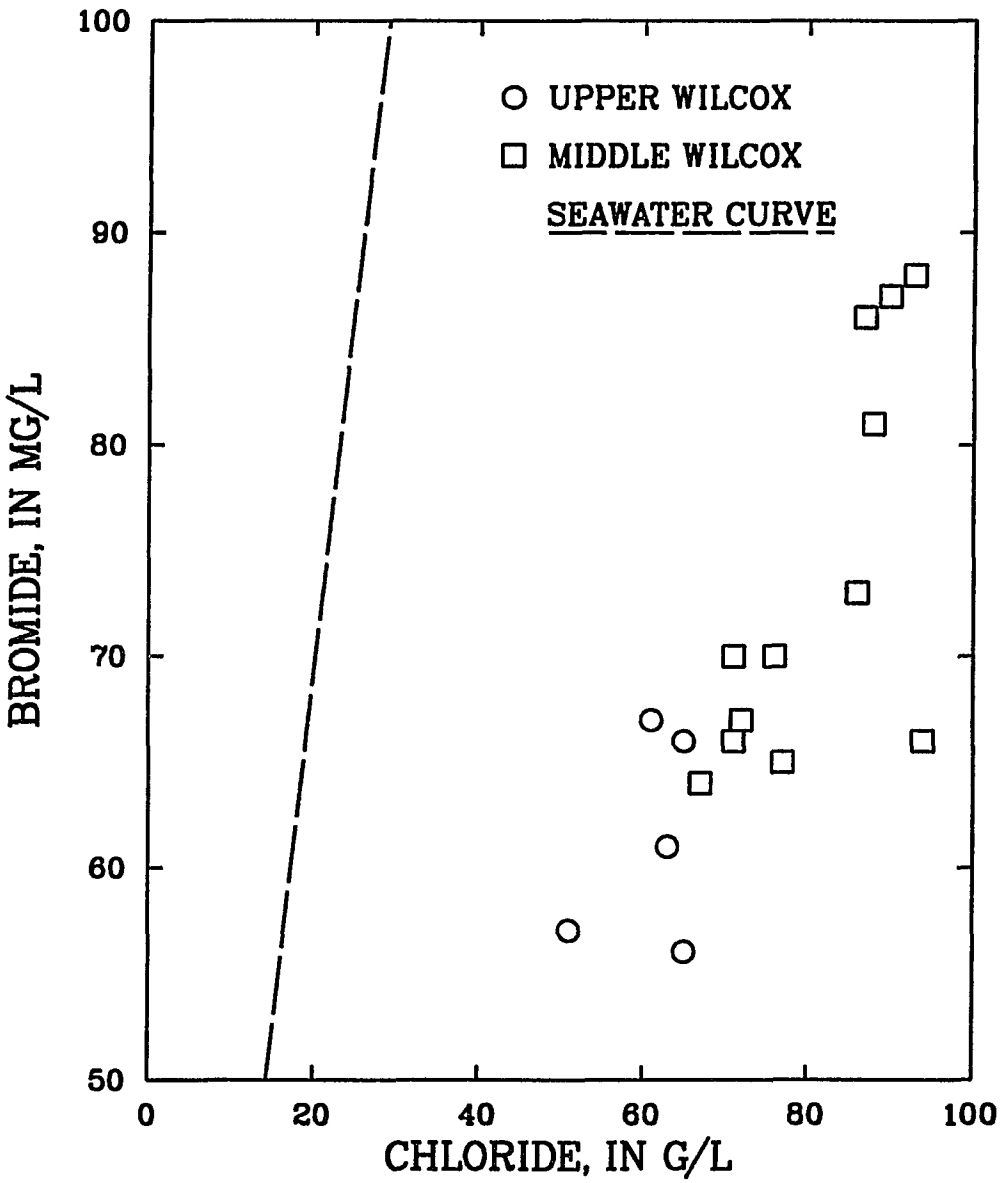


Figure 3.13 Concentrations of Br as a function of concentrations of Cl in the upper and middle units of the Wilcox Aquifer.

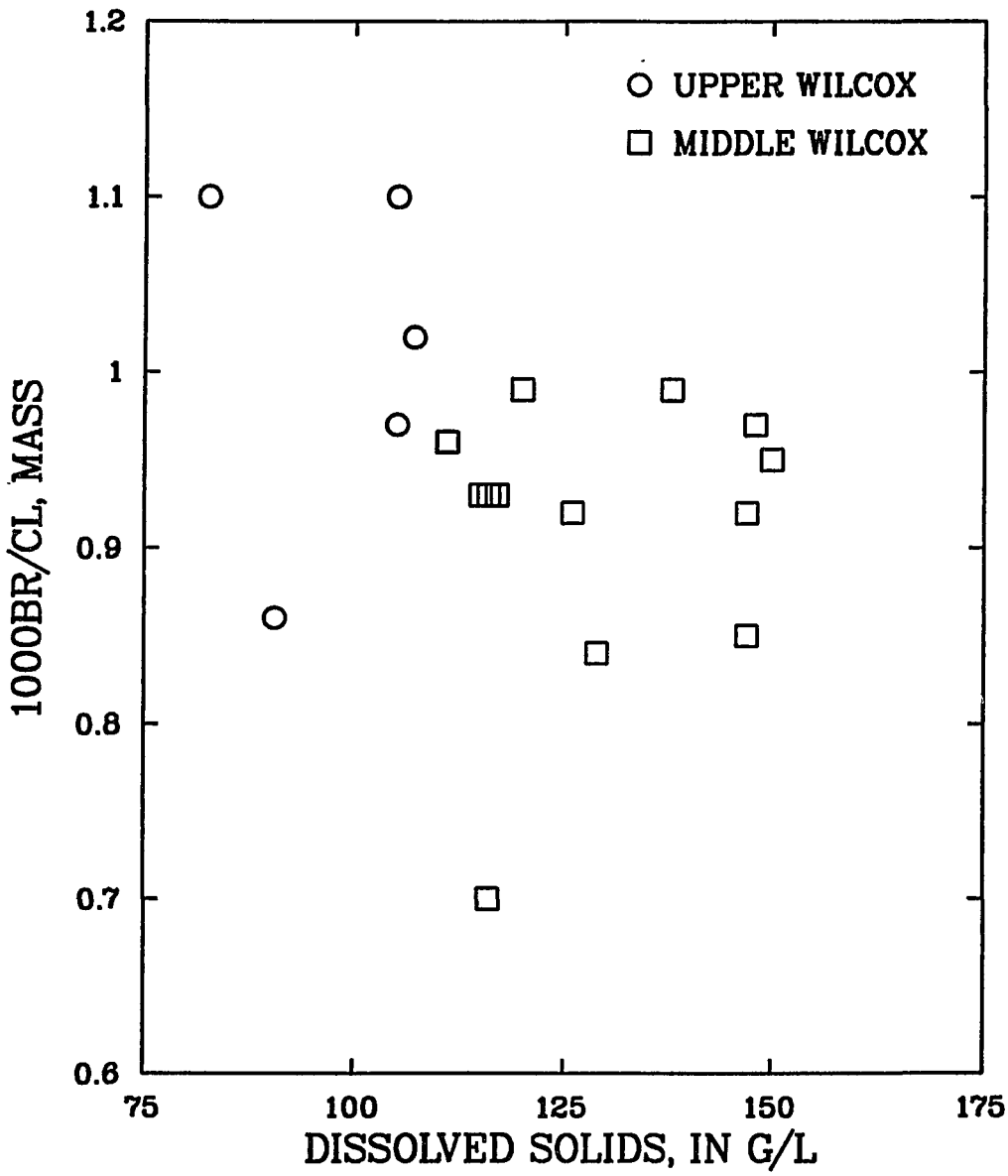


Figure 3.14 Br/Cl ratio as a function concentrations of dissolved solids in the upper and middle units of the Wilcox Aquifer.

fall between approximately 0.85×10^{-3} and 1.1×10^{-3}. These values fall at the low-Br end of compositions observed for brines from sediments of Tertiary age in the Gulf Coast as reported by Land and others (1988).

Isotopes of O, H, and Sr

Values of $\delta^{18}O$ are approximately -1 o/oo and values of δD range from approximately -13 to -15 o/oo in all sampled oil wells (fig. 3.15). Neither $\delta^{18}O$ or δD show any systematic change with increasing concentrations of dissolved solids. The isotopic composition of brines and saline waters from the Wilcox aquifer is offset from the meteoric water line (fig. 3.16). Average reported values of $\delta^{18}O$ and δD in meteoric water from the Gulf Coast range from approximately -4.5 to -3.5 o/oo and -18 to -22 o/oo, respectively, as summarized by (Posey and others, 1985). Brines and saline waters from the study area are enriched in ^{18}O and slightly enriched in D with respect to reported compositions of Gulf Coast meteoric water.

Values of $^{87}Sr/^{86}Sr$ in brines and saline waters from the Wilcox aquifer fall between 0.7072 and 0.7081 and increase with increasing concentrations of dissolved solids (fig. 3.17). The $^{87}Sr/^{86}Sr$ values of less-saline waters sampled from the Wilcox aquifer is consistent with that of mid-Jurassic seawater (0.7068 to 0.7072) as given by Burke and others (1982).

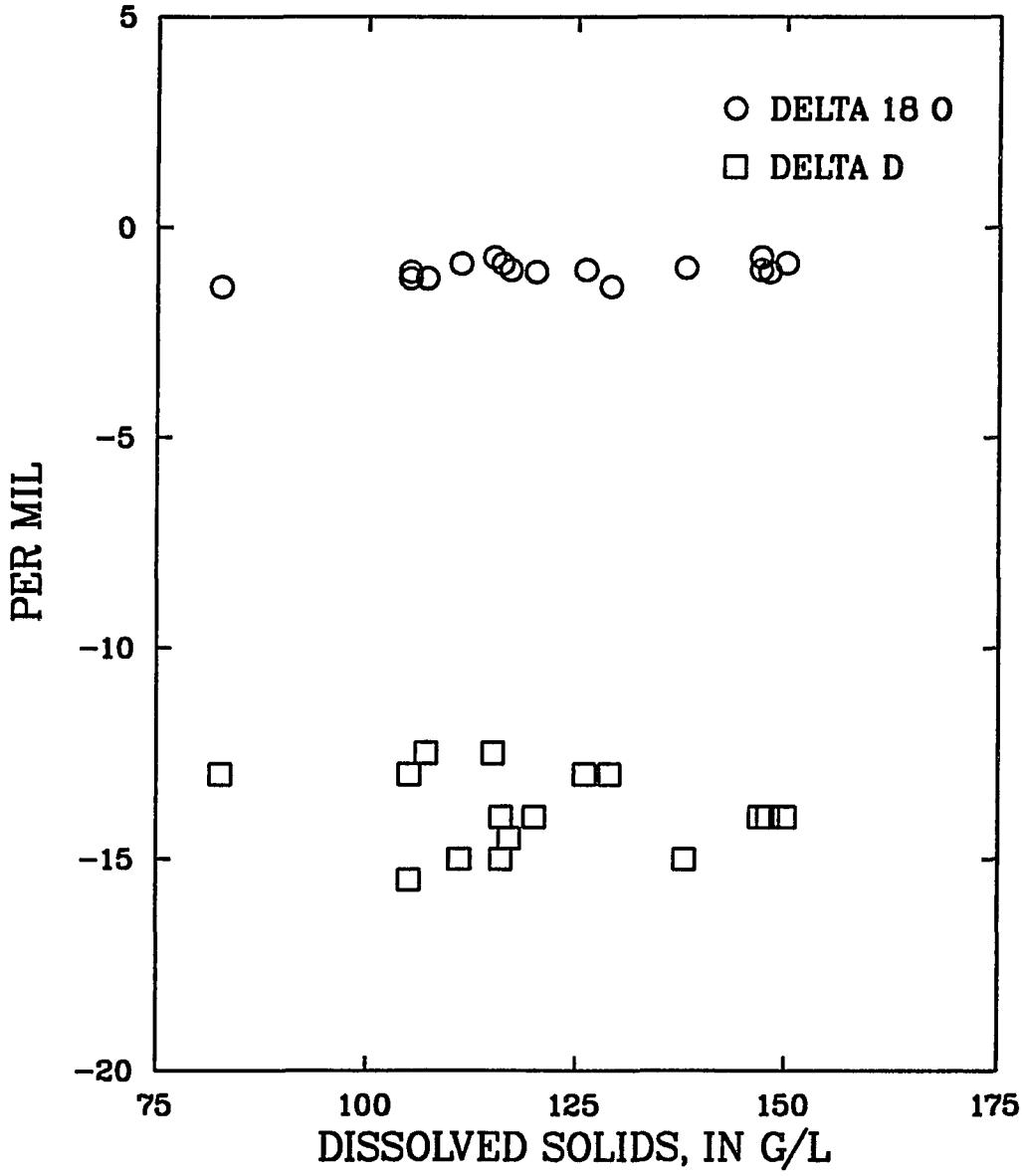


Figure 3.15 Values of $\delta^{18}O$ and δD as a function of dissolved solids concentrations.

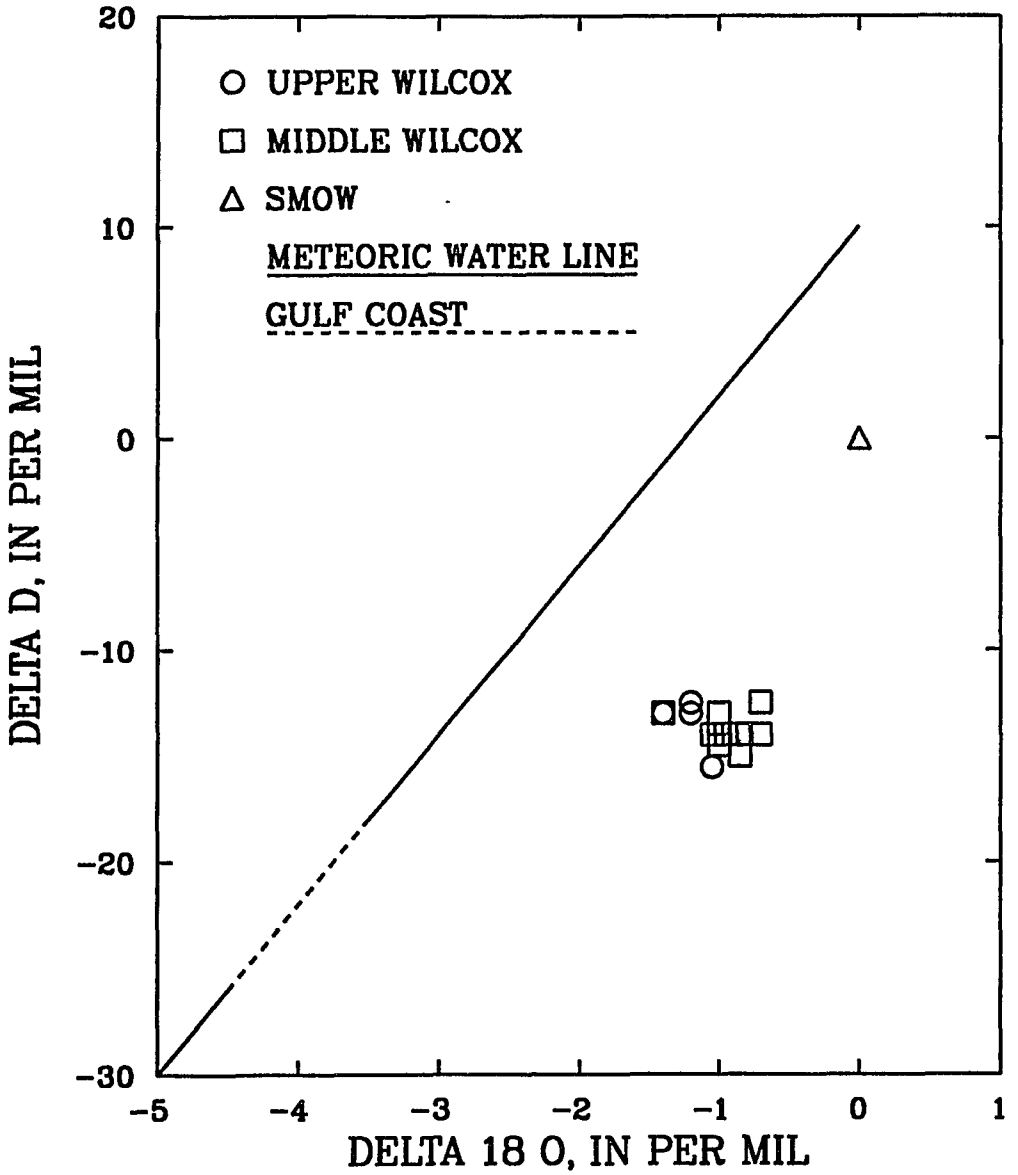


Figure 3.16 Values of δD as a function of $\delta^{18}O$ in the upper and middle units of the Wilcox Aquifer. Meteoric water line from Craig (1961). Values of Gulf Coast meteoric water as summarized by Posey and others (1985).

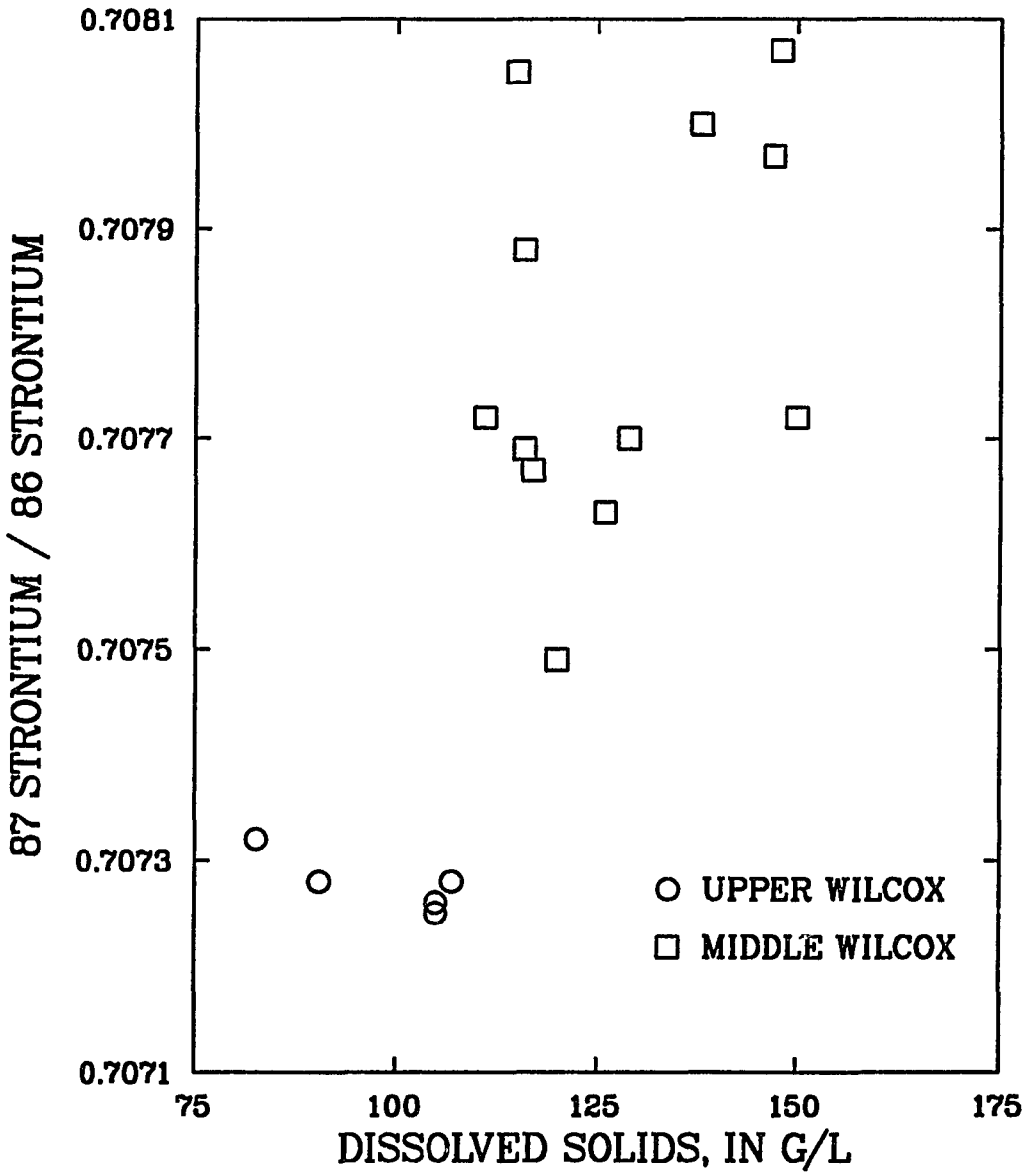


Figure 3.17 $^{87}Sr/^{86}Sr$ as a function of dissolved solids concentrations in the upper and middle units of the Wilcox Aquifer.

MINERAL-STABILITY CALCULATIONS

The stabilities of several rock-forming minerals were calculated to assess the potential for water-rock interaction in controlling the elemental and isotopic composition of brines and saline water in the Wilcox aquifer. Stabilities of non-silicate minerals were modeled in terms of precipitation-dissolution reactions. Stabilities of silicate minerals were modeled in terms of alteration reactions written to conserve Al. Table 3.1 lists all modeled reactions. Subsurface temperatures used in mineral-stability calculations were assigned based on the regional geothermal gradient (fig 3.2). Potential loss of volatiles during sample collection prevent reliable measurement of in-situ pH. As such, values of pH were assigned based on the assumption of equilibrium with calcite.

Stabilities of minerals included in dissolution-precipitation reactions (reactions 1 through 5) were calculated in terms of the saturation index (SI) using PHREEQE (Parkhurst and others, 1980) and PHRQPITZ (Plummer and others, 1988). Because PHRQPITZ does not calculate activities of aqueous silica species, the SI of quartz and amorphous silica (reactions 4 and 5) were calculated exclusively using PHREEQE. Positive values of the SI indicate favorable conditions for mineral precipitation while negative values indicate favorable conditions for mineral dissolution. An SI of 0 ± 0.2 indicates apparent

Table 3.1 Modeled dissolution-precipitation and alteration reactions at one bar with associated log K values for alteration reactions at 50°C, 75°C, and 100°C. Alteration reactions have been written to conserve Al. Values of log K for reactions 6, 9, 10, and 12 were taken from Kaiser (1984). Values of log K for the remaining alteration reactions were calculated using free energy, enthalpy, and heat capacity data from Helgeson (1969) and Robie and others (1979).

1. $CaSO_4.2H_2O = Ca^{2+} + SO_4^{2-}$
   (gypsum)

2. $SrSO_4 = Sr^{2+} + SO_4^{2-}$
   (celestite)

3. $SrCO_3 = Sr^{2+} + CO_3^{2-}$
   (strontianite)

4. $SiO_2 + H_2O = H_4SiO_4$
   (quartz)

5. $SiO_2 + H_2O = H_4SiO_4$
   (amorphous silica)

6. $Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_8 + 3.45H_2O + 1.30H^+ =$
   (plagioclase (An30))

   $0.65Al_2Si_2O_5(OH)_4 + 0.70Na^+ + 0.30Ca^{2+} + 1.40H_4SiO_4$
   (kaolinite)

$\log K_{50^oC} = 4.3 \quad \log K_{75^oC} = 3.9 \quad \log K_{100^oC} = 3.6$

(table con'd.)

7. $Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_8 + 1.1H_2O + 1.2H^+ =$
(plagioclase (An30))

$0.56Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 0.70Na^+ + 0.20Ca^{2+} + 0.6H_4SiO_4$
(Ca-smectite)

$\log K_{50^oC} = 3.91 \quad \log K_{75^oC} = 3.59 \quad \log K_{100^oC} = 3.28$

8. $Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_8 + 1.1H_2O + 1.2H^+ =$
(plagioclase (An30))

$0.56Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 0.52Na^+ + 0.30Ca^{2+} + 0.60H_4SiO_4$
(Na-smectite)

$\log K_{50^oC} = 4.83 \quad \log K_{75^oC} = 4.41 \quad \log K_{100^oC} = 4.00$

9. $Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_8 + 0.6Na^+ + 1.2\ H_4SiO_4 =$
(plagioclase (An30))

$1.3NaAlSi_3O_8 + 0.30Ca^{2+} + 2.4H_2O$
(albite)

$\log K_{50^oC} = 4.7 \quad \log K_{75^oC} = 4.3 \quad \log K_{100^oC} = 3.8$

10. $KAlSi_3O_8 + Na^+ = NaAlSi_3O_8 + K^+$
(microcline) (albite)

$\log K_{50^oC} = -2.66 \quad \log K_{75^oC} = -2.35 \quad \log K_{100^oC} = -2.07$

11. $KAlSi_3O_8 + 0.11Mg^{2+} + 3.10H_2O + 0.52H^+ =$
(microcline)

$0.43K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2 + 0.74K^+ + 1.50H_4SiO_4$
(illite)

$\log K_{50^oC} = 0.72 \quad \log K_{75^oC} = 1.04 \quad \log K_{100^oC} = 1.31$

(table con'd.)

12. $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$ (illite) $+ 1.10H^+ + 3.15H_2O =$

$0.65Al_2Si_2O_5(OH)_4$ (kaolinite) $+ 0.60K^+ + 0.25Mg^{2+} + 1.20H_4SiO_4$

$\log K_{50^oC} = -3.9 \quad \log K_{75^oC} = -4.1 \quad \log K_{100^oC} = -4.4$

13. $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$ (illite) $+ 0.33Na^+ + 0.17H_4SiO_4 + 0.68H^+ =$

$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (Na-smectite) $+ 0.60K^+ + 0.25Mg^{2+} + 0.68H_2O$

$\log K_{50^oC} = 5.70 \quad \log K_{75^oC} = 5.34 \quad \log K_{100^oC} = 5.00$

14. $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$ (illite) $+ 0.17Ca^{2+} + 0.17H_4SiO_4 + 0.68H^+ =$

$0.56Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (Ca-smectite) $+ 0.60K^+ + 0.25Mg^{2+} + 0.68H_2O$

$\log K_{50^oC} = 4.07 \quad \log K_{75^oC} = 3.90 \quad \log K_{100^oC} = 3.73$

15. $Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (Ca-smectite) $+ 0.33Na^+ =$

$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (Na-smectite) $+ 0.17Ca^{2+}$

$\log K_{50^oC} = 0.35 \quad \log K_{75^oC} = 0.23 \quad \log K_{100^oC} = 0.13$

16. $KAl_3Si_3O_{10}(OH)_2$ (muscovite) $+ H^+ + 1.5H_2O = 1.5Al_2Si_2O_5(OH)_4$ (kaolinite) $+ K^+$

$\log K_{50^oC} = 10.5 \quad \log K_{75^oC} = 9.79 \quad \log K_{100^oC} = 9.12$

(table con'd.)

17. $KAl_3Si_3O_{10}(OH)_2$ (muscovite) $+ 0.33Mg^{2+} + 1.55H_4SiO_4 =$

$0.43K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$ (illite) $+ 0.22K^+ + 0.44H^+ + 2.60H_2O$

$\log K_{50^oC} = 7.72$ $\log K_{75^oC} = 7.85$ $\log K_{100^oC} = 7.97$

equilibrium between mineral and solution (Moldovanyi and Walter, 1992). Calculation of the SI is discussed in detail in Appendix III. Because PHRQPITZ does not calculate values of the equilibrium constant (K) for strontianite or celestite, values of K used in these SI calculations were taken from PHREEQE. Calculations of SI values using ionic activities calculated using PHRQPITZ and K values calculated using PHPREEQE are designated as mixed.

Reaction diagrams, showing the stability fields of minerals listed in table 3.1, were constructed for all alteration reactions (reactions 6 through 17). Calculation of values of K from thermodynamic data and the correction of values of K for the effects of pressure and temperature are discussed in detail in Appendix III. Because PHRQPITZ (Plummer and others, 1988) does not calculate activities of aqueous silica species only PHREEQE (Parkhurst and others, 1980) was used to calculate the activities of aqueous species in reactions 4 through 10.

Calculations of SI as a function of ionic strength of solution show gypsum, celestite, and strontianite (fig. 3.18) and amorphous silica (fig. 3.19) to be undersaturated and quartz (fig. 3.19) to be slightly oversaturated in brines and saline waters from the Wilcox aquifer. Data plot between the 50°C and 100°C phase boundaries between illite and Ca-smectite (fig. 3.20) suggesting equilibrium between these mineral phases. Data plot parallel to but slightly offset from phase boundaries between microcline and albite

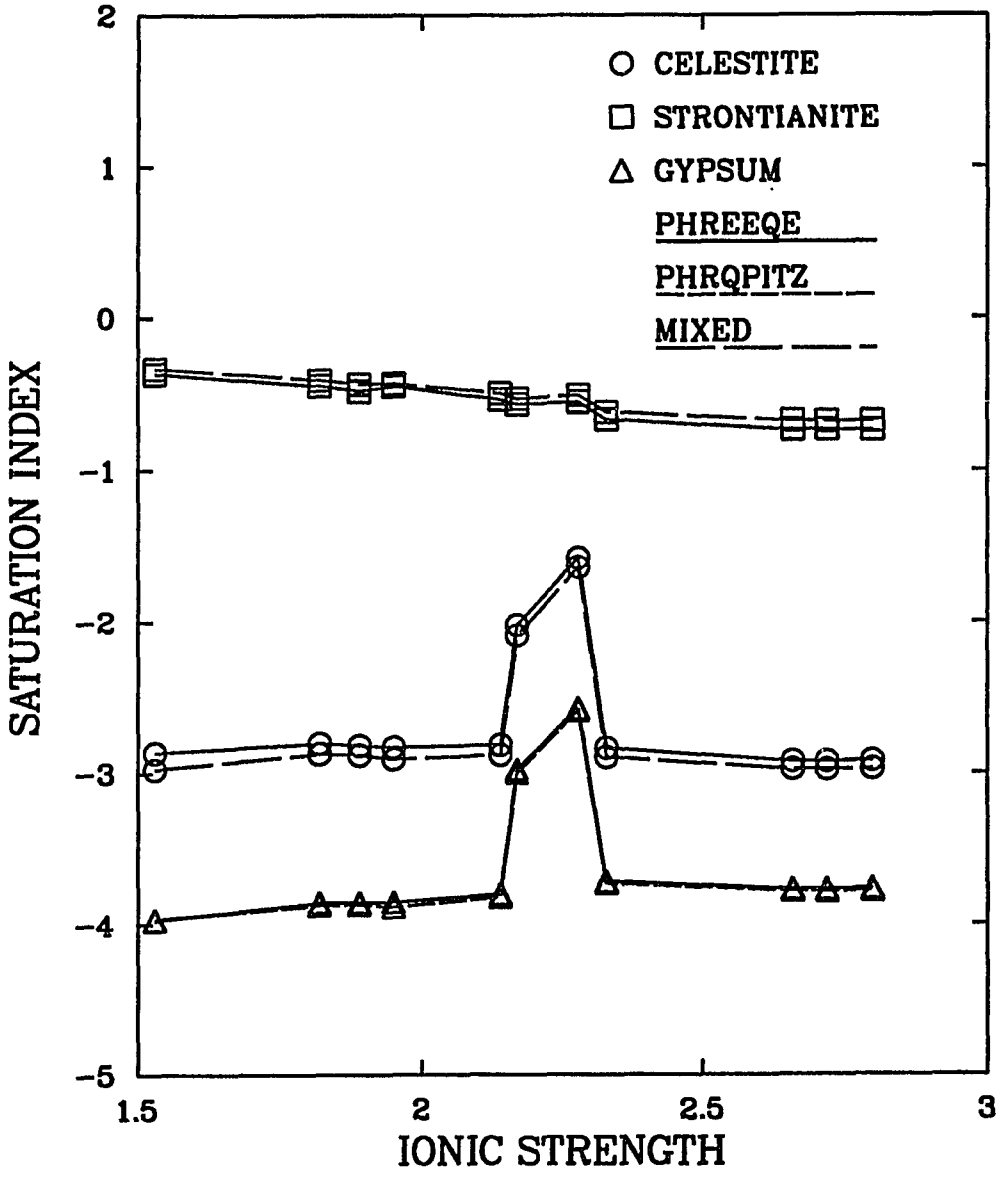


Figure 3.18 Saturation index of celestite, strontianite, and gypsum.

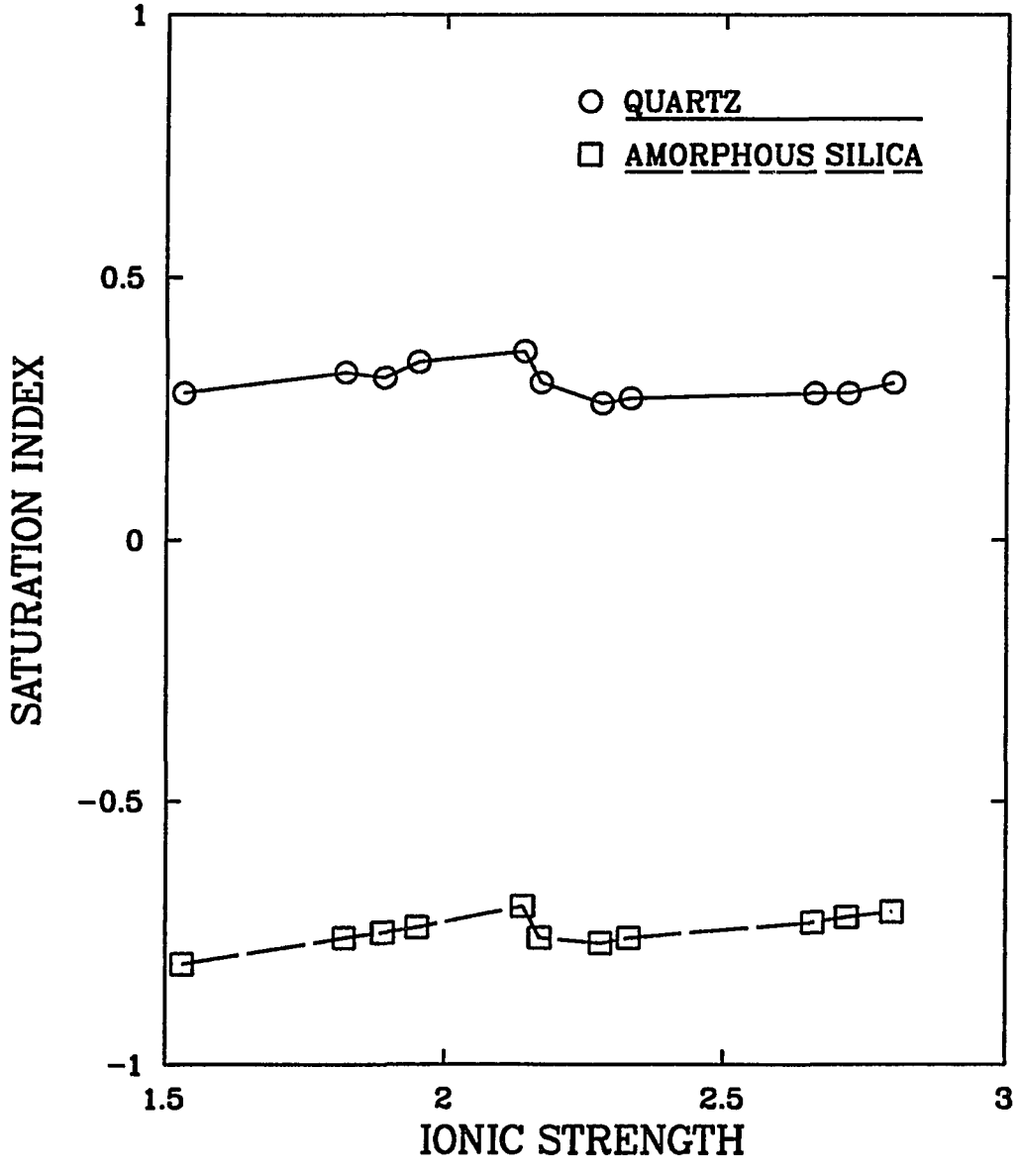


Figure 3.19 Saturation index of quartz and amorphous silica.

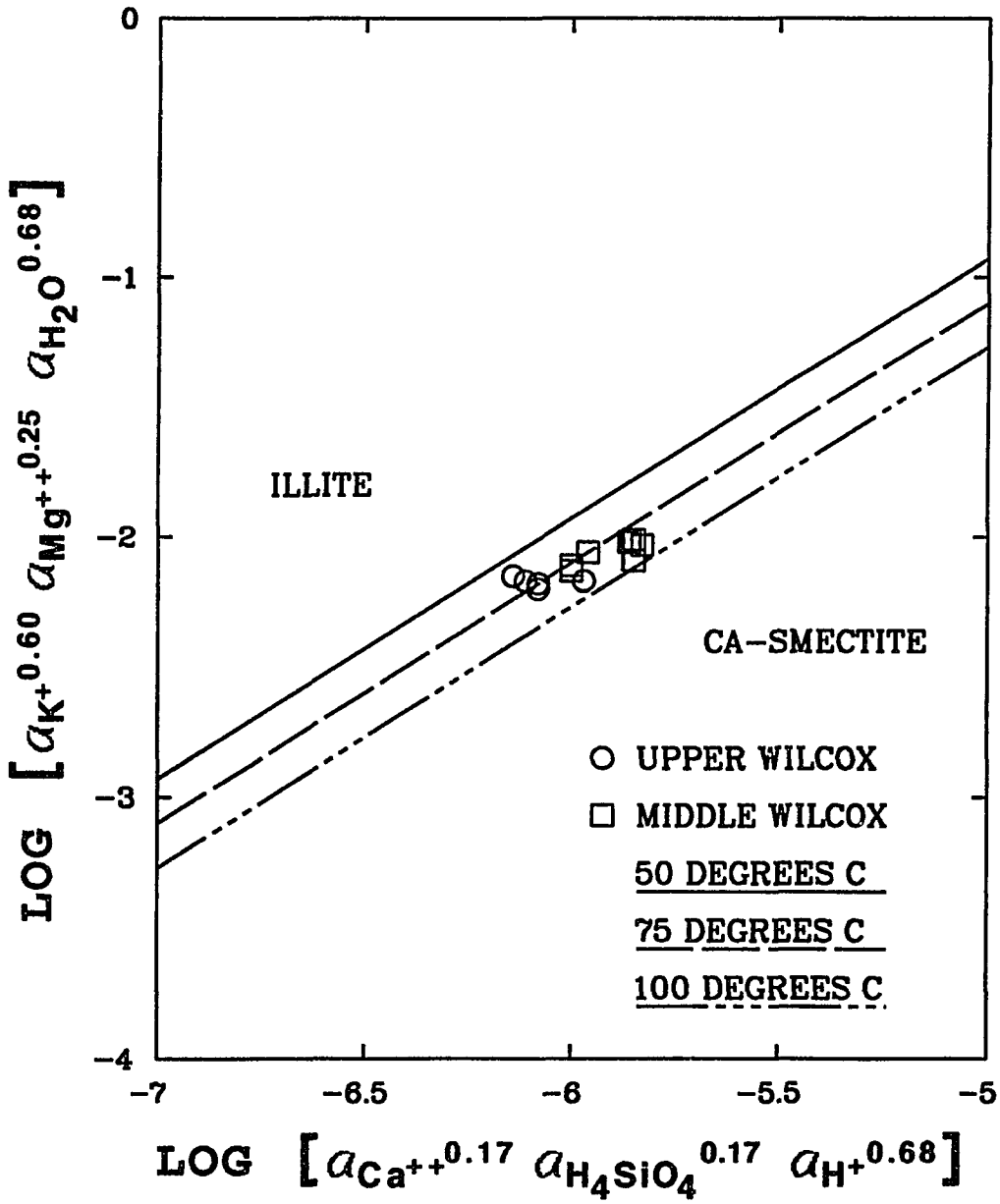


Figure 3.20 Activities of solutes in the upper and middle units of the Wilcox Aquifer plotted on the stability fields of illite and Ca-smectite.

(fig. 3.21), plagioclase (An30) and kaolinite (fig. 3.22), and plagioclase (An30) and Na-smectite (fig. 3.23) indicating that equilibrium conditions may be approached in these reactions. Slight differences in the compositions of minerals used to calculate log K values and the compositions of minerals present in the subsurface may account for the offset from the phase boundaries in figures 3.21, 3.22, and 3.23. Abundant authigenic kaolinite is present in the Wilcox of eastern central Louisiana (Ezat Heydari, Basin Research Institute, Louisiana State University, personal communication, 1993). The presence of authigenic kaolinite supports the theoretical prediction of equilibrium between plagioclase (An30) and kaolinite. No evidence exists to suggest an approach to equilibrium for other alteration reactions in table 3.1.

CONTROLS ON SOLUTE AND ISOTOPIC ABUNDANCES

Mineral Equilibria

Concentrations of dissolved species shown in figures 3.11 and 3.12 increase with increasing concentrations of dissolved solids with the exceptions of alkalinity, Mg, and Sr. The shape of the dissolved solids versus alkalinity curve for values between approximately 80 and 110 g/L dissolved solids suggests consumption of alkalinity by a chemical such as precipitation of calcite.

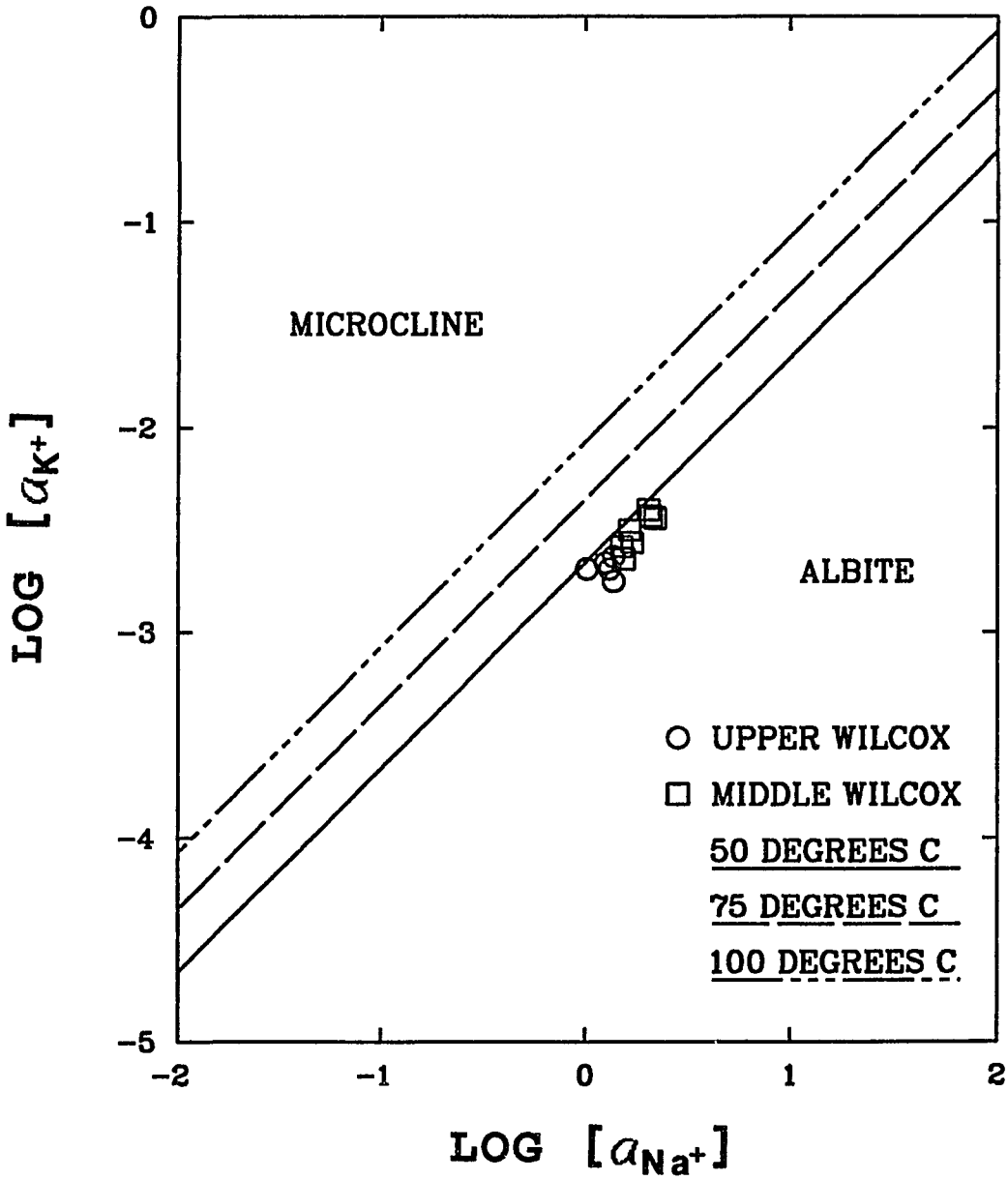


Figure 3.21 Activities of solutes in the upper and middle units of the Wilcox Aquifer plotted on the stability fields of microcline and albite.

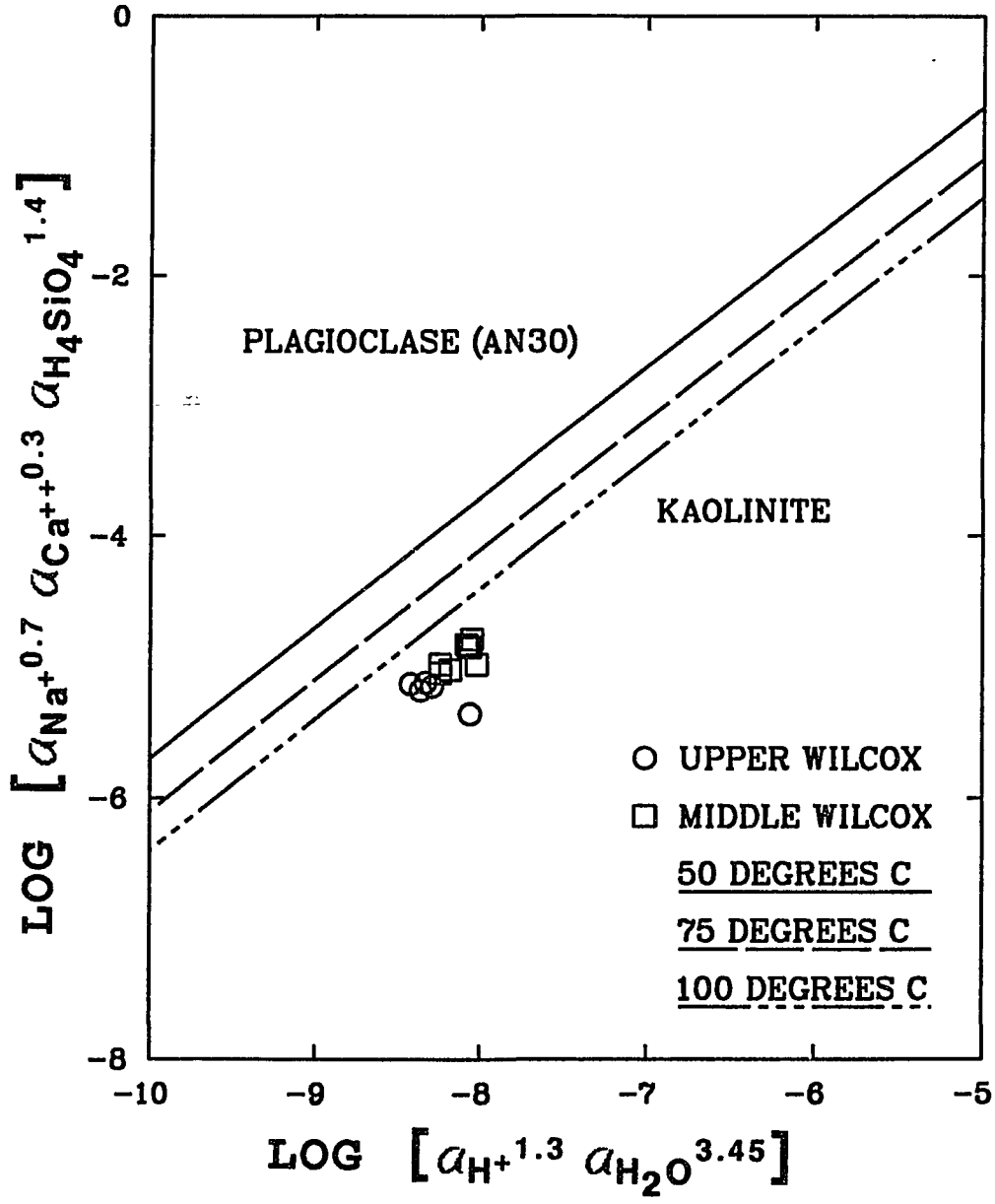


Figure 3.22 Activities of solutes in the upper and middle units of the Wilcox Aquifer plotted on the stability fields of plagioclase (An30) and kaolinite.

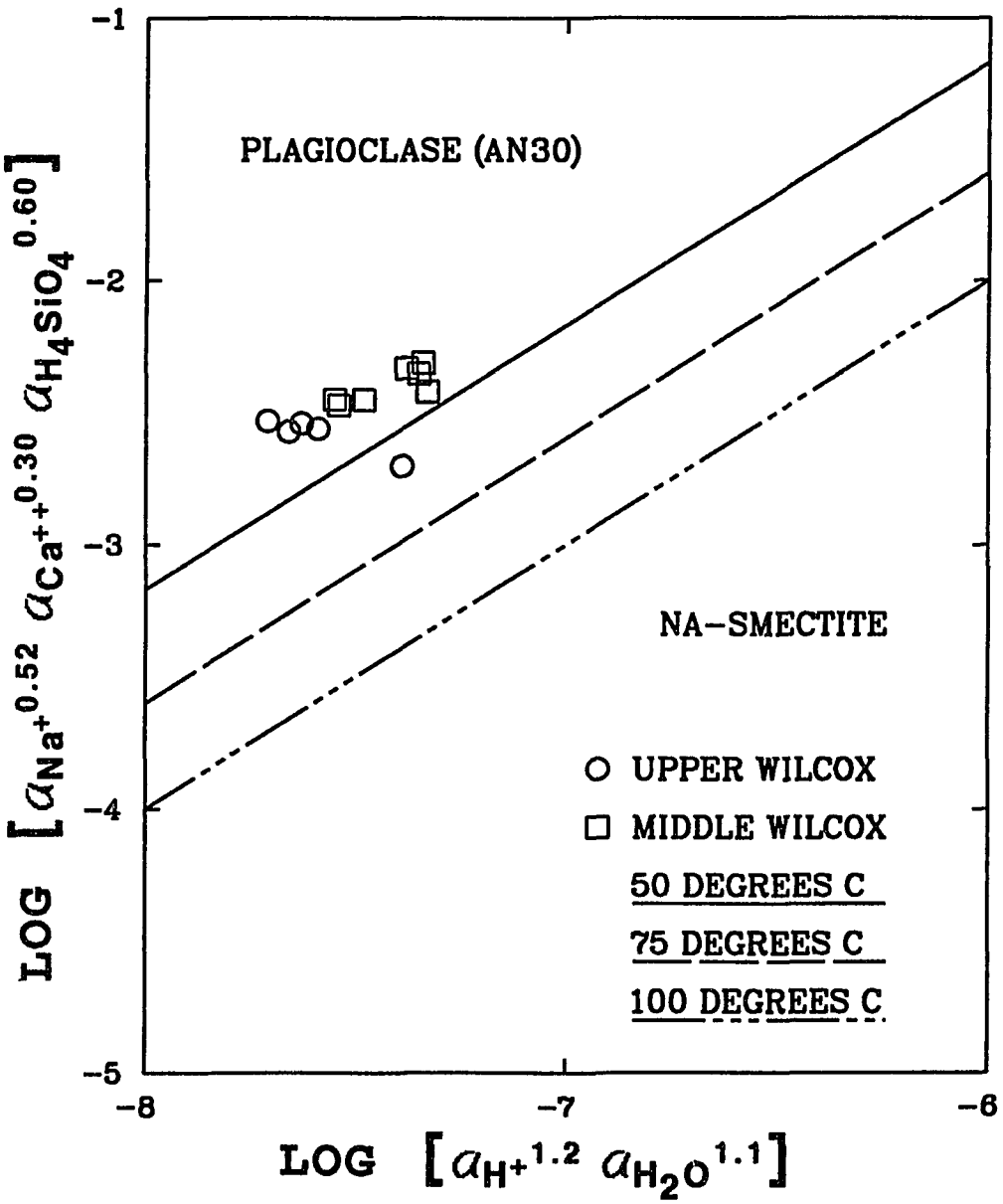


Figure 3.23 Activities of solutes in the upper and middle units of the Wilcox Aquifer plotted on the stability fields of plagioclase (An30) and Na-smectite.

The relative constancy of dissolved-Sr concentrations over the entire range of dissolved solids concentrations suggests rock buffering of Sr. Both gypsum and celestite are strongly undersaturated with respect to brines and saline waters of the Wilcox aquifer and therefore could not be responsible for buffering of dissolved Sr. Stontianite is apparently undersaturated to slightly undersaturated in Wilcox brines and saline waters. However, the SI of strontianite is strongly dependent on pH. A decrease in pH of approximately 0.5 from that calculated by assuming equilibrium with calcite would bring brines and saline water of the Wilcox aquifer into equilibrium with strontianite (fig. 3.24). Strontianite is known to occur in hydrothermal settings (Hurlbut and Klein, 1974) and in salt dome caprocks (Walker, 1974; Rovik, 1978; Saunders and others, 1988). The occurrence of strontianite, however, is rare in other geologic settings. As such, it is unlikely that Sr concentrations in brines and saline waters of the Wilcox aquifer are buffered by strontianite.

Katz (1973) presented a temperature-dependent partitioning coefficient ($\lambda(T)$) for Mg on the surface of precipitating calcite as a function of the molalities of Mg and Ca in solution under conditions of 25^{o} to 90^{o}C at 1 bar and $P_{CO_2} = 10^{-2.5}$. Values of $\lambda(T)$ increased linearly with temperature over the experimental range indicating that Mg partitioning into calcite was favored by increasing temperature. This relationship has the form

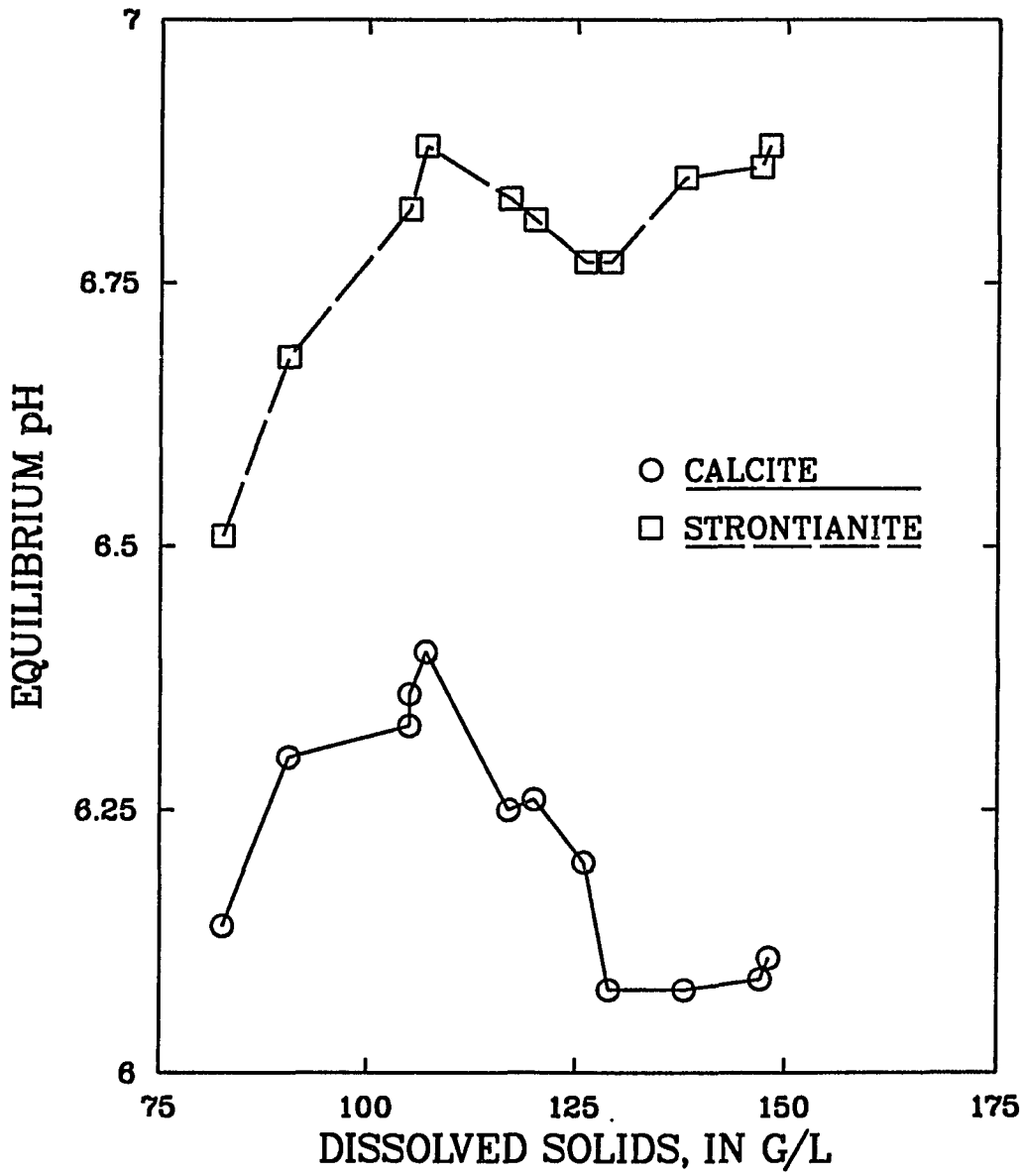


Figure 3.24 Equilibrium pH values for calcite and strontianite in the Wilcox Aquifer.

$$(M_{Mg}/M_{Ca})_{surf} = \lambda(T)\ (M_{Mg}/M_{Ca})_{aq} \qquad \text{equation 3.2}$$

where the subscript surf refers to molar ratios on the surface of precipitating calcite and the subscript aq refers to molal ratios in aqueous solution. Rewriting in terms of activities, equation 3.2 becomes

$$(M_{Mg}/M_{Ca})_{surf} = \lambda(T)\ (\gamma_{Ca}/\gamma_{Mg})_{aq}(a_{Mg}/a_{Ca})_{aq} \qquad \text{equation 3.3}$$

Assuming $(\gamma_{Ca}/\gamma_{Mg})_{aq} \approx 1$ in the low ionic-strength solutions used in the experiments of Katz (1973), equation 3.3 can be simplified to

$$(M_{Mg}/M_{Ca})_{surf} = \lambda(T)\ (a_{Mg}/a_{Ca})_{aq} \qquad \text{equation 3.4}$$

which is applicable in higher ionic-strength waters. The mole % $MgCO_3$ in calcite which could be precipitating from selected brines and saline waters in the Wilcox aquifer is shown in figure 3.25. Values of mole % $MgCO_3$ in precipitating calcite were calculated using equation 3.4 and activities of Ca and Mg were calculated using both PHREEQE and PHRQPITZ. Values of $MgCO_3$ in precipitating calcite range from 10 to 11 mole % in brines and saline waters having dissolved solids concentrations less than approximately 110 g/L and 5 to 7 mole % where dissolved solids concentrations exceed approximately 110 g/L.

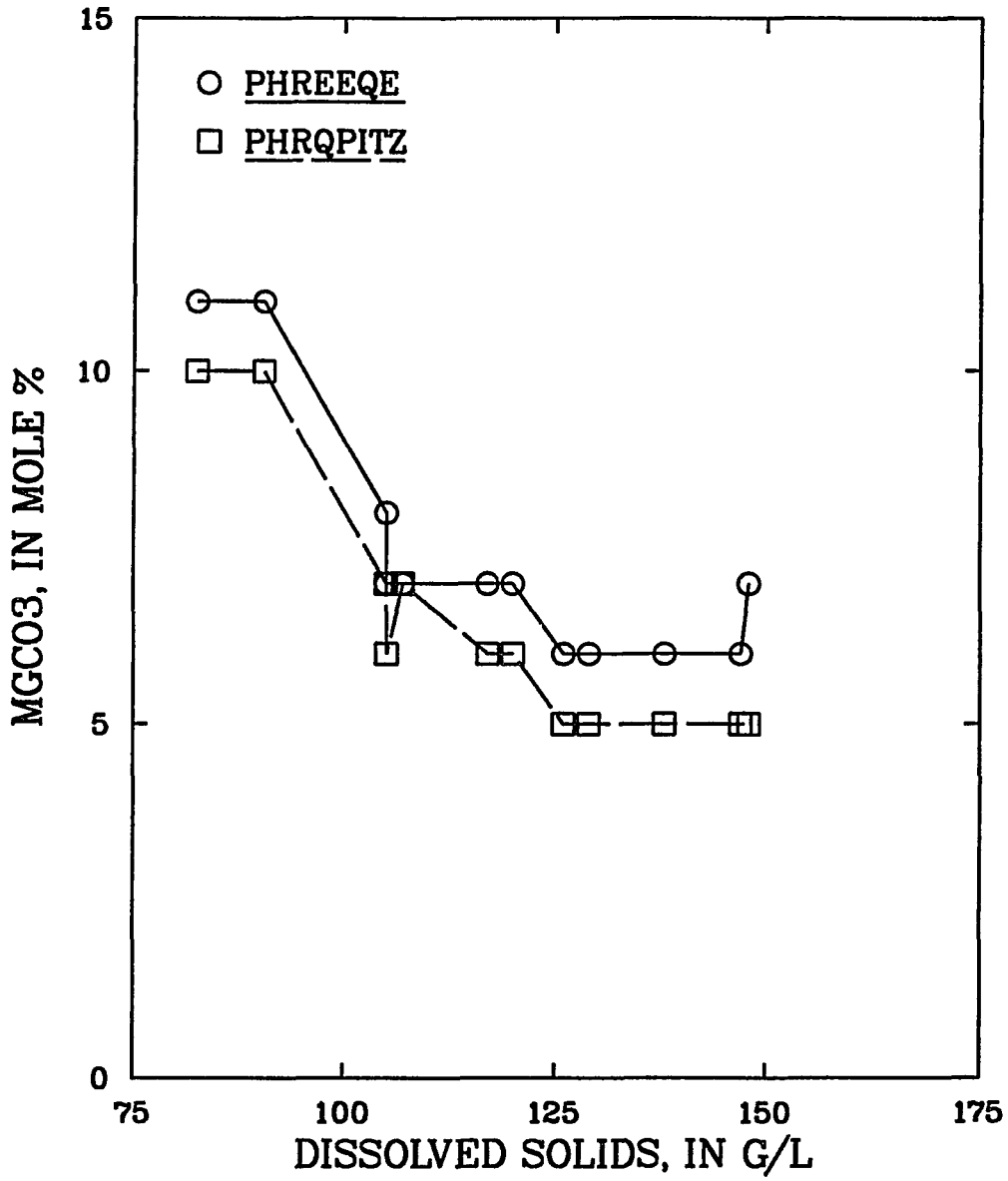


Figure 3.25 Predicted mole-% $MgCO_3$ in precipitating calcite as a function of dissolved solids concentrations.

Experimental data at 25°C shows that calcite with greater than approximately 5 mole % $MgCO_3$ is less stable than pure calcite (Plummer and Mackenzie, 1974). Experimental data on the solubility of Mg-calcite at temperatures higher than 25°C apparently do not exist in the literature. Likewise, thermodynamic data on Mg-calcite which would allow calculation of stabilities at elevated temperatures are lacking. If one assumes that the relationship established at 25°C between Mg content and calcite stability holds at higher temperatures, calcite containing 5 to 7 mole % $MgCO_3$ may buffer waters at a higher pH than those shown in figure 3.24 for pure calcite.

The work of Pingitore and others (1986) shows that Sr incorporation into precipitating calcite at 25°C and approximately 1 bar is strongly inhibited in the presence of dissolved NaCl. However, the effects of temperature and pressure on the partitioning of Sr into precipitating calcite are unknown. Buffering of Sr concentrations and buffering of pH at values higher than those calculated by assuming equilibrium with calcite could possibly be accomplished by a $(Ca,Mg,Sr)CO_3$ solid solution.

Decreasing concentrations of dissolved Mg with increasing concentrations of dissolved solids is in opposition to trends shown by all other dissolved species with the exception of Sr. By analogy with Mg-calcite, Mg may be more strongly partitioned into a $(Ca,Mg,Sr)CO_3$ solid solution with increasing temperature. Such behavior could

explain the apparent decrease in dissolved Mg concentrations with increasing concentrations of dissolved solids.

Br preferentially partitions into the aqueous phase during recrystallization of halite leaving the aqueous phase enriched in Br relative to the recrystallizing salt. The typical value for Gulf Coast diapiric salt is approximately 50 mg Br/kg halite (Land and others, 1988). Using data from Land and others (1988), brines and saline waters from the Wilcox aquifer have Br/Cl ratios consistent with formation from recrystallizing salt containing approximately 15 mg Br/kg halite. Br/Cl ratios in brines and saline waters of the Wilcox aquifer are lower than that expected to be formed on recrystallization of salt containing 50 mg Br/kg halite. This indicates that the Br/Cl ratios of brines and saline waters from the Wilcox aquifer have been controlled, in part, by dissolution rather than recrystallization of halite.

Values of $\delta^{18}O$ and δD are shifted by approximately +3 o/oo and +6 o/oo, respectively, with respect to reported values of Gulf Coast meteoric water as summarized by Posey and others (1985). The $\delta^{18}O$ and δD values of brines and saline waters in the Wilcox aquifer are highly similar to values in brines hosted by Eocene to Pliocene sediments from depths of less than approximately 2500 m (8000 ft) located some 60 km (40 mi) south of the Concordia Parish study area (Posey and others, 1985). Using their more extensive data base, Posey and others (1985) have concluded that observed

$\delta^{18}O$ shifts were not caused by evaporation of water. They invoke water-rock interaction as a mechanism to introduce ^{18}O into solution. The relative constancy of $\delta^{18}O$ values of brines and saline waters in Tertiary aquifers of both eastern central and south central Louisiana suggests the possibility that O isotopes may be buffered by water rock interaction.

Extrapolation of trends present in the $\delta^{18}O$ and δD data sets of Posey and others (1985) allowed them to hypothesize that δD values reported for Gulf Coast meteoric water may actually be lighter than those characteristic of south central Louisiana. If brines and saline waters in the Wilcox aquifer have a strong meteoric component, this could also explain the δD shift observed in the Concordia Parish study area.

Perhaps the most significant aspect of $\delta^{18}O$ and δD values of brines and saline waters in the Wilcox aquifer to the north and in Eocene to Pliocene sediments to the south is their similarity rather than the exact mechanism(s) which produced the observed isotopic signatures. The similarity suggests that brines and saline waters in aquifers of Tertiary age in south and central Louisiana, where not influenced by infiltration of water from the geopressured zone, may form a relatively isotopically-homogenous body having no radical differences in their histories of water-rock interaction. A more extensive data base than is

currently available is needed to verify or refute this hypothesis.

Ground-Water Flow

Alteration of silicate minerals and illite dissolution of gypsum, celestite, and strontianite have been identified as possible sources of Sr in brines and saline waters of the Wilcox aquifer in eastern central Louisiana. It is very likely that gypsum, celestite, and strontianite exist in meaningful amounts only in the salt dome/diapir or caprock environments. Anhydrite also exists in association with salt domes/diapirs and caprock and should also be considered as a possible source of Sr. While any of these alteration or dissolution reactions may be sources of Sr to solution they do not account for the distribution of Sr isotopes in brines and saline waters of the Wilcox aquifer.

The distribution of Sr isotopes in evaporite minerals of salt basins in the Gulf Coast was discussed in detail in Chapter I. The occurrence of evaporite minerals having $^{87}Sr/^{86}Sr$ ratios more radiogenic than mid-Jurassic seawater in the Gulf Coast Salt Dome Basin is well documented in the literature. Similarly, evaporite minerals in the Mississippi and North Louisiana Salt Dome Basins typically have $^{87}Sr/^{86}Sr$ ratios characteristic of mid-Jurassic seawater. Lateral ground-water flow is generally from the south into the lower and middle units (figs. 1.9 and 1.10) and from the

northwest into the upper unit (fig. 1.11) of the Wilcox aquifer in eastern central Louisiana. These lateral flow patterns would bring brines or saline waters which had had opportunity to interact with salt- or shale-hosted minerals having $^{87}Sr/^{86}Sr$ values more radiogenic than mid-Jurassic seawater in the Gulf Coast Salt Dome Basin into the lower and middle units of the Wilcox aquifer. Upward flow from the lower into the middle unit of the Wilcox aquifer could also introduce brines or saline waters which had interacted with more-radiogenic Sr-bearing minerals. Lateral ground-water flow would bring brines and saline waters which had interacted with minerals having $^{87}Sr/^{86}Sr$ values similar to mid-Jurassic seawater in the North Louisiana Salt Dome Basin into the upper unit of the Wilcox aquifer.

Values of $^{87}Sr/^{86}Sr$ plotted as a function of 1/Cl are shown in figure 3.26. A best-fit line has been drawn through the data points using the least-squares linear regression technique. Although a good deal of scatter is present, all but two data points fall within one standard deviation of the best-fit line. If one assumes that Sr more radiogenic than mid-Jurassic seawater is being added to solution by dissolution of evaporite minerals then the solution into which radiogenic-Sr-bearing minerals are dissolving may be at or near halite saturation. On this assumption, the best-fit line and lines representing one standard deviation have been extended to a 1/Cl value representing halite saturation at 100^{o}C calculated using the equation of Potter and others,

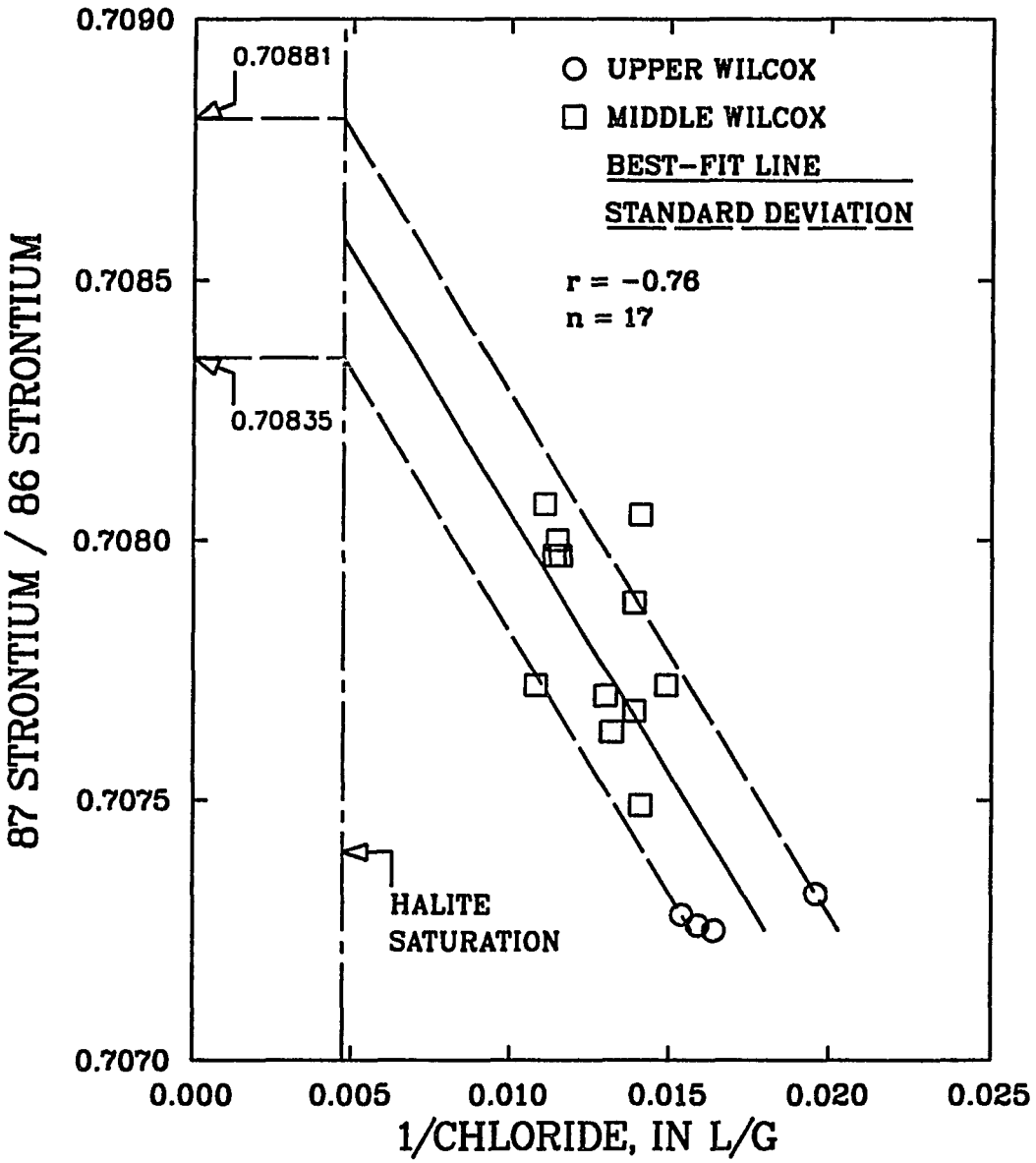


Figure 3.26 $^{87}Sr/^{86}Sr$ as a function of 1/Cl in the upper and middle units of the Wilcox Aquifer.

1977). The temperature of 100°C was chosen based on the subsurface temperature near the first down dip occurrence of massive salt in the Wilcox aquifer as reported by Eversull (1984). The graphical approach shown in figure 3.26 yields $^{87}Sr/^{86}Sr$ values of 0.7084 to 0.7088 for minerals contributing radiogenic Sr to solution. Values of $^{87}Sr/^{86}Sr$ for minerals contributing the more radiogenic component of Sr into solution (assuming dissolution of these minerals into water at or near halite saturation) overlap those reported for anhydrite and barite in the Gulf Coast Salt Dome Basin of coastal east Texas (0.7071-0.7094) (Posey and others, 1987). Values from a single well in the Gulf Coast salt Dome Basin of offshore Louisiana (0.7091-0.7098) (Land and others, 1988) are more radiogenic than the bulk of values for coastal east Texas and Mississippi. These values almost certainly do not represent the entire range of $^{87}Sr/^{86}Sr$ in salt dome/diapir materials for offshore Louisiana. They do indicate, however, that $^{87}Sr/^{86}Sr$ values for offshore Louisiana could be expected to be more radiogenic than mid-Jurassic seawater. Salt dome materials having $^{87}Sr/^{86}Sr$ values characteristic of mid-Jurassic seawater are common in the North Louisiana and Mississippi Salt Dome Basins.

The relationship observed between values of $^{87}Sr/^{86}Sr$ and 1/Cl is consistent with a mixture of a more-saline end-member having a range of $^{87}Sr/^{86}Sr$ values within those documented to occur in the Gulf Coast Salt Dome Basin with a

less-saline end-member having a range of $^{87}Sr/^{86}Sr$ values similar to mid-Jurassic seawater characteristic of the North Louisiana Salt Dome Basin. These end-members exist in the middle and upper units of the Wilcox aquifer in eastern central Louisiana. Cross-formational mixing of water in the upper and middle units could produce the results shown in figure 3.26.

It is possible that the more radiogenic component of Sr could be derived from dissolution or alteration of shale-hosted silicate minerals in the down-dip Wilcox. If this were the case, however, the observed $^{87}Sr/^{86}Sr$ ratio of brines at a 1/Cl value characteristic of halite saturation would be difficult to explain.

Considerable scatter is present in the $^{87}Sr/^{86}Sr$ as a function of 1/Cl relationship (fig. 3.26). Posey and others (1985) have noted that individual oil fields in south Louisiana typically have unique Sr-isotope relationships. This may arise form the influence of one dominant source of Sr such as a nearby salt dome/diapir or shale unit. Many such sources, likely having individual but overlapping ranges of $^{87}Sr/^{86}Sr$ values, exist in the massive salt deposits of the Gulf Coast Salt Dome Basin. Samples of a heterogenous mixture of waters flowing away from each of these sources would potentially carry $^{87}Sr/^{86}Sr$ values characteristic of the entire range of source values. If $^{87}Sr/^{86}Sr$ values in these waters were plotted against a value such as 1/Cl scatter in the apparent mixing

relationship would result both from the ranges of values in sources of radiogenic Sr and from variations in dissolved Cl concentrations due to differential degrees of dilution by less saline water. The scatter observed in figure 3.26 could be explained by a heterogenous mixture of waters containing Sr contributions from multiple sources in both the more- and less-radiogenic end-members and by differential dilution producing waters of somewhat variable dissolved-Cl concentrations.

The Big Shale is a transgressive marine shale unit which has been discussed by Galloway (1968), McCulloh and Eversull (1986), and Lowry (1987). Hydrologically, it approximates the base of the upper unit of the Wilcox aquifer. The northern limit of the Big Shale coincides with a general transition in oil producing reservoirs from the middle to the upper Wilcox Group. This suggests that the presence of the Big Shale inhibits upward vertical movement of oil (Funayama, 1990). This resistance to the flow of oil raises the possibility that the Big Shale may also act as an aquitard between the upper and middle units of the Wilcox aquifer.

If the Big Shale acts as a aquiclude, the results shown in figure 3.26 could result from mixing of brines and saline waters having $^{87}Sr/^{86}Sr$ values characteristic of mid-Jurassic seawater introduced into the middle unit of the Wilcox aquifer by lateral flow from the northwest with brines and saline waters having more radiogenic $^{87}Sr/^{86}Sr$

values introduced into the middle unit by lateral flow from the south. Lateral flow into the middle unit from the northwest is not predicted by the flow model of Williamson and others (1990). This apparent contradiction could be attributed to the low resolution of the regional-scale model arising from the necessarily coarse discritization.

Distributions of salinity and density along cross-section A-A′ (fig. 3.4) are typically more laterally stratified than along cross-section B-B′ (fig. 3.7). The general absence of the Big Shale along B-B′ may allow for enhanced vertical mixing between ground-waters in the upper and middle units of the Wilcox aquifer. This enhanced vertical mixing between waters having relatively high alkalinities in the upper unit and relatively high concentrations of dissolved Ca in the middle unit could cause carbonate mineral precipitation. Precipitation of carbonate minerals could explain the observed rapid decrease in alkalinity with increasing concentrations of dissolved solids up to dissolved solids concentrations of approximately 110 g/L.

CHAPTER SUMMARY

Brines and saline waters in the Wilcox aquifer of eastern central Louisiana are Na-Cl type waters with dissolved solids concentrations ranging from 83 to 150 g/L. Concentrations of dissolved solids generally increase with

depth. Concentrations of all determined species increase with increasing concentrations of dissolved solids with the exceptions of alkalinity, Mg, and Sr. Alkalinity decreases rapidly with increasing concentrations of dissolved solids up to approximately 110 g/L. Concentrations of dissolved Mg decrease with increasing concentrations of dissolved solids while Sr shows little or no change. Values of the Br/Cl ratio fall between approximately 0.85×10^{-3} and 1.1×10^{-3}. Values of $\delta^{18}O$ and δD are approximately -1 o/oo and -13 to -15 o/oo, respectively, and show no change with increasing concentrations of analytical dissolved solids. These values of $\delta^{18}O$ and δD represent shifts of approximately +3 o/oo and +6 o/oo, respectively, from reported values of Gulf Coast meteoric water.

The rapid decrease in alkalinity with increasing concentrations of dissolved solids can be explained by precipitation of calcite on enhanced mixing of brines and saline water in the upper and middle units of the Wilcox aquifer in the absence of the Big Shale. The relative constancy of dissolved Sr suggests that rock buffering may control Sr concentrations in solution. Precipitation of a $(Ca,Mg,Sr)CO_3$ solid solution may place an upper limit on the concentration of Sr in aqueous solution. The apparent decrease in dissolved Mg concentrations with increasing concentrations of dissolved solids may reflect increased partitioning of Mg into a $(Ca,Mg,Sr)CO_3$ solid solution with increasing temperature.

The observed +3 o/oo shift in $\delta^{18}O$ over the entire range of dissolved solids concentrations may also reflect the effects of rock buffering. The observed +6 o/oo shift in δD values may be explained by the presence of meteoric water heavier than values previously reported for the Gulf Coast.

Apparent chemical equilibrium exists of is closely approached between illite and Ca-smectite, microcline and albite, plagioclase (An30) and kaolinite, and plagioclase (An30) and Na-smectite. The presence of authigenic kaolinite in the Wilcox Aquifer of eastern central Louisiana supports the theoretical prediction of plagioclase (An30) kaolinite equilibrium.

The Gulf Coast regional average for diapiric salt is approximately 50 mg Br/kg halite. Brines and saline waters in the Wilcox aquifer have Br/Cl ratios expected on formation from recrystallizing salt containing approximately 15 mg Br/kg halite. This indicates that the Br/Cl ratios of brines and saline waters have been determined, in part, by dissolution rather than recrystallization of halite.

The relationship between $^{87}Sr/^{86}Sr$ and 1/Cl is consistent with a heterogenous mixture of a more-saline end-member having $^{87}Sr/^{86}Sr$ values more radiogenic than mid-Jurassic seawater and a less-saline end-member having $^{87}Sr/^{86}Sr$ values similar to mid-Jurassic seawater. The regional patterns of ground-water flow allows more-radiogenic Sr to be derived from the Gulf Coast Salt Dome

Basin and less radiogenic Sr to be derived from the North Louisiana Salt Dome Basin.

Distributions of SP-derived salinity and density as well as geochemical evidence indicates that vertical mixing between the upper and middle units of the Wilcox aquifer is greatly enhanced in the absence of the Big Shale. The Big Shale, where present, may act as an aquitard between the upper and middle units of the Wilcox aquifer.

CHAPTER IV

ORIGIN AND MOVEMENT OF BRACKISH WATER IN THE ALLUVIAL AQUIFER OF MOREHOUSE PARISH, LOUISIANA AND SOUTHERN CHICOT COUNTY, ARKANSAS

PURPOSE

Sanford (1973) reported the occurrence of a relatively small area of brackish water in the Alluvial Aquifer of northeastern Morehouse Parish, Louisiana. Crop failures, associated with salinity of alluvial water used for irrigation, spread over a larger area in 1988 than the area of brackish water mapped by Sanford (1973) (J.C. Stevens, Louisiana Agricultural Extension Service, personal communication, 1988). The 1988 area of crop failures indicated that the area of brackish water described by Sanford (1973) may have expanded over the intervening 15 years. The general direction of lateral ground-water flow in eastern Morehouse Parish is southwestward with strong easterly components near the Boeuff River (Sanford, 1973). The apparent expansion of brackish water to the southwest suggested geologic rather than hydrologic controls may be governing the direction of brackish water expansion. Because the potential for density-driven flow exists, the relationship between the paleotopogrphy at the base of the

Alluvial Aquifer and the distribution of brackish water in the Alluvial Aquifer is of particular interest.

A band of water in the Alluvial Aquifer having elevated salinities (based on Cl concentrations of greater than 100 mg/L) extends northeastward from Franklin into West Carroll Parish, Louisiana (Whitfield, 1975) (fig. 1.8). This band of elevated salinities (based on dissolved solids concentrations of 500 to 1,000 mg/L) also extends into southern and central Arkansas (Boswell and others, 1968). An area of anomalous salinity (dissolved solids concentrations greater than 1,000 mg/L) within the band of elevated salinities was reported by Boswell and others (1968) in southern Chicot County, Arkansas. This area of anomalous salinity was mapped in greater detail by Fitzpatrick (1985) on the basis of elevated Cl concentrations. The detailed geologic and hydrologic controls on these areas of elevated salinity are unknown. The relationship, if any, between brackish water in the Alluvial Aquifer of eastern Morehouse Parish and the band of elevated salinities shown in figure 1.8 is also unknown.

The purpose of this chapter is to evaluate the hydrogeologic controls on the occurrence of water having elevated salinities in the Alluvial Aquifer of eastern Morehouse Parish, Louisiana and southern Chicot County, Arkansas. A particular concern is the relationship of these areas in Morehouse Parish with the band of elevated

salinities present on a regional scale in the Alluvial Aquifer.

DESCRIPTION OF THE STUDY AREA

The Morehouse Parish study area includes northeastern and south central Morehouse Parish, Louisiana and adjoining areas of southern Chicot County, Arkansas (figs. 1.1 and 4.1). Land surface has a mean elevation of approximately 27 m (90 ft) above sea level and very little local topographic relief.

HYDROGEOLOGY OF THE ALLUVIAL AQUIFER

The generalized geologic column, including the Louann Salt and all younger formations within the study area, is shown in figure 4.2. The Pleistocene Mississippi River alluvial deposits, which make up the Alluvial Aquifer, unconformably overlie the Tertiary Cockfield Formation throughout the study area. Thickness of the Mississippi River alluvial deposits ranges from approximately 27 m (90 ft) over paleotopographic highs on the Cockfield Formation to more than 46 m (150 ft) over paleotopographic lows (Saucier, 1967; Sanford, 1973). Mississippi River alluvial deposits which infill the paleotopographic lows contain a greater fraction of coarse sand and gravel than those which cover paleotopographic highs (Sanford, 1973).

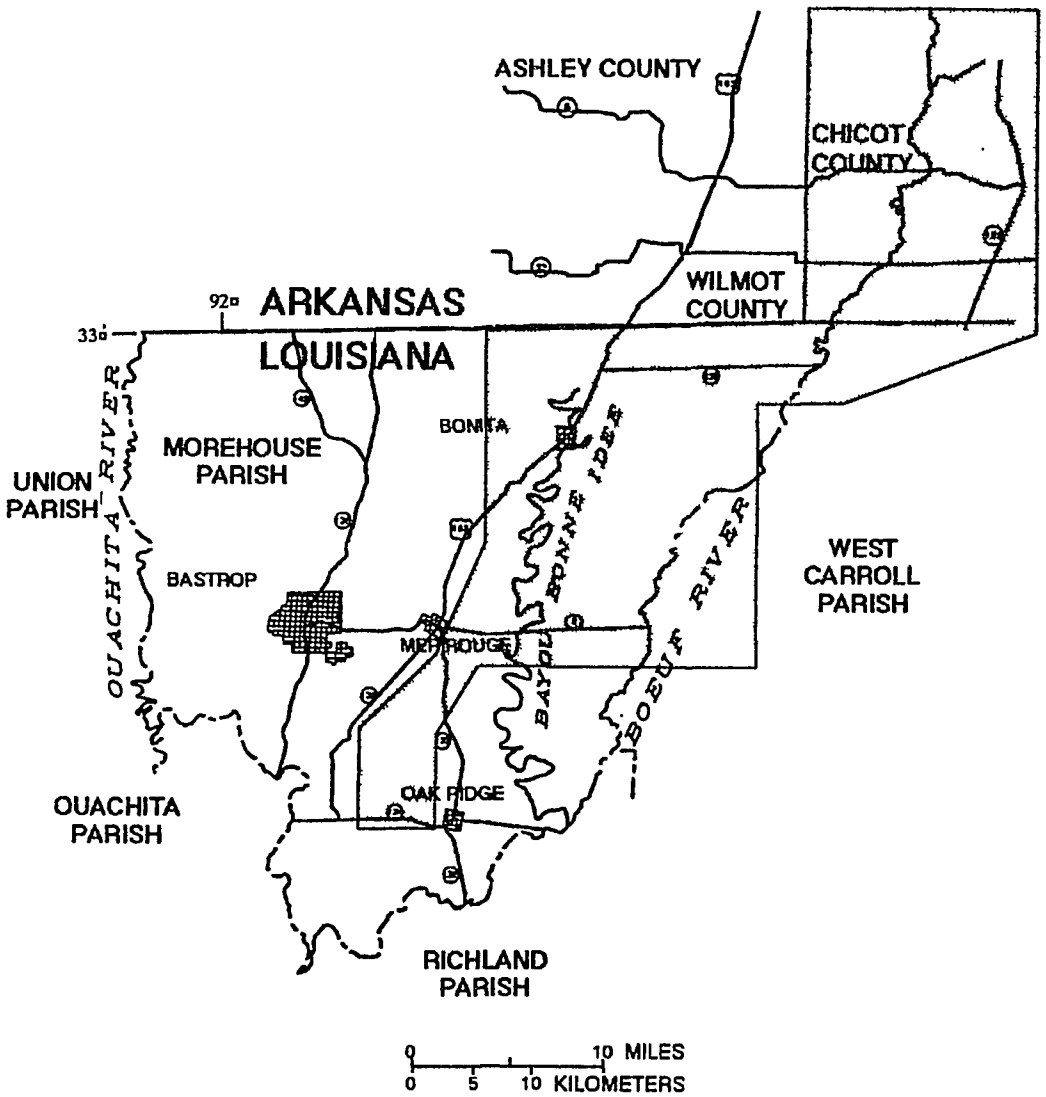


Figure 4.1 Location of the Morehouse Parish study area.

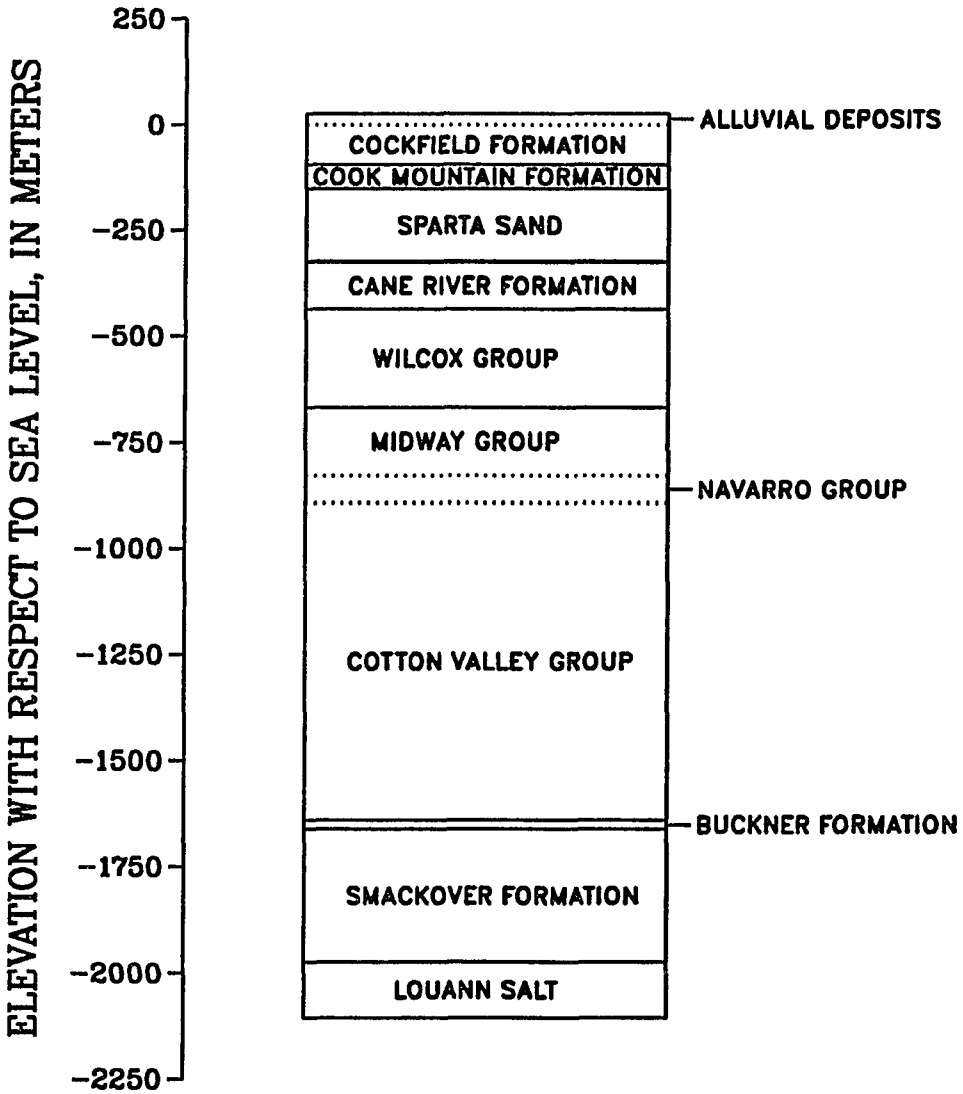


Figure 4.2 Generalized geologic column showing the Louann Salt and younger formations in the Morehouse Parish study area (modified from Eversull, 1984 and Smoot, 1989).

Lateral ground-water flow in the Alluvial Aquifer is generally to the south. Locally, the presence of rivers and streams or large amounts of ground-water withdrawal can affect the direction of ground-water flow. Rivers such as the Boeuf can seasonally act as line discharge or line recharge (Sanford, 1973).

Recharge through the top of the Alluvial Aquifer, excluding contributions from rivers and streams, was estimated to be between 1.3 and 3.8 cm per year (0.51 and 1.5 inches per year) over the study area. This recharge may result from direct infiltration of rainfall in areas where sandy sediments extend to the surface, or leakage from a perched water table in areas where clays and silts overlie the Alluvial Aquifer. A net recharge of up to 1.3 cm per year (0.5 inches per year) occurs by upward flow through the base of the Alluvial Aquifer in the study area (Ackerman, 1989).

The Alluvial Aquifer of Morehouse Parish typically contains a Ca-Mg-HCO_3 type water. Areas of the Alluvial Aquifer within northeastern Morehouse Parish contain water of higher Cl concentrations (Sanford, 1973).

DATA COLLECTED

Ground-water samples were taken from 46 irrigation wells: 38 in eastern Morehouse Parish and 8 in southern Chicot County, all screened in the Alluvial Aquifer. These

wells are typically screened over intervals of up to 12 m (40 ft) and can produce a mixture of subsurface waters from a density-stratified system. Thus, the concentration of any constituent present in water produced from these wells does not necessarily reflect the highest concentration present in the aquifer. Two test holes were drilled in northeastern Morehouse Parish and examined using induction resistivity and spontaneous potential logs.

The results of all chemical analyses of ground-water samples collected from the study area are given in table 4.1. Most constituents show a concentration range of one order of magnitude or greater.

FRESH AND BRACKISH WATER

Areal Distribution of Brackish Water

Figure 4.3 identifies and shows the location of all wells sampled in the study area. Figure 4.4 shows concentrations of dissolved solids in water samples plotted on the mapped elevation above sea level of the unconformable contact between the top of the Cockfield Formation and the base of the overlying Mississippi River alluvial deposits.

Paleotopographic features on the top of the Cockfield Formation suggest two roughly parallel northeast-southwest trending fluvial channels. In eastern Morehouse Parish, wells producing ground water with concentrations of

Table 4.1 Chemical analyses of brackish and fresh waters from irrigation and monitor wells in Morehouse Parish and Chicot County.

Well Number	Date (YY-MM-DD)	Temp. (°C)	Specific Conductance (µS/cm @ 25°C)	pH	Alkalinity (mg/L HCO3)	Ca (mg/L)	Mg (mg/L)	Ba (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO4 (mg/L)	SiO2 (mg/L)	Sr (mg/L)	Br (mg/L)	Dissolved Solids (mg/L)
Mo-381	89-08-22	20.0	1370	7.1	476	120	38	0.36	110	4.0	140	110	32	0.95	0.35	734
Mo-397	89-08-11	20.5	990	7.1	457	100	34	0.42	53	2.1	65	37	27	0.78	0.23	454
Mo-399	89-08-11	20.5	790	7.1	422	85	26	0.40	41	2.3	28	17	27	0.49	0.09	414
Mo-411	88-12-01	18.0	3300.	7.1	566	290	86	0.40	270	5.9	740	200	28	2.4	1.6	1910
Mo-435	88-12-02	17.0	750	7.2	415	77	23	0.56	54	3.3	36	17	35	0.67	0.14	442
Mo-446	88-11-29	17.0	1460	7.1	522	140	34	0.50	120	3.1	180	90	35	0.68	0.74	865
Mo-515	88-11-10	- -	- -	7.2	417	90	24	0.37	23	1.7	15	14	34	0.48	0.12	402
Mo-588	88-11-30	17.0	680	7.0	390	87	22	0.46	30	2.3	31	42	36	0.57	0.27	415
Mo-632	88-11-09	20.0	3360	6.8	546	260	94	0.20	310	4.2	620	450	28	1.6	2.2	2010
Mo-633	88-11-11	17.0	1230	7.4	451	62	17	0.29	180	2.6	190	8.3	29	0.48	0.58	709
Mo-634	88-11-29	18.0	1550	7.4	488	92	26	0.43	200	2.5	270	19	30	0.66	0.78	872
Mo-635	88-11-30	18.0	2010	7.3	512	130	38	0.66	240	3.8	410	20	32	0.89	1.1	1100
Mo-636	88-12-01	17.0	3000	7.2	610	270	91	0.10	270	4.6	540	390	28	1.6	1.3	1840
Mo-637	88-12-01	19.0	2180	7.2	507	190	63	0.50	170	4.6	380	160	28	1.5	0.92	1240
Mo-638	88-12-02	18.0	3250	7.1	527	260	96	0.20	300	4.0	610	360	30	1.3	2.1	1880
Mo-658	89-08-10	20.5	930	7.1	439	98	38	0.12	43	1.9	36	83	33	0.35	0.08	495
Mo-659	89-08-10	21.0	1140	7.2	419	110	39	0.13	64	2.2	81	120	31	0.43	0.20	602
Mo-660	89-08-18	19.5	2000	7.0	483	160	57	0.17	150	4.3	240	230	31	1.1	0.67	1120
Mo-661	89-08-17	20.0	1190	7.1	436	110	27	0.60	96	3.8	160	5.0	36	0.76	0.47	532
Mo-662	89-08-18	20.5	710	7.1	417	93	25	0.51	23	2.3	9.5	20	37	0.63	0.08	264
Mo-663	89-08-17	20.5	765	7.1	435	110	22	0.54	26	1.5	18	13	37	0.67	0.08	381

(table con'd.)

Well Number	Sample Date (YY-MM-DD)	Temp. (°C)	Specific Conductance (µS/cm @ 25°C)	pH	Alkalinity (mg/L HCO3)	Ca (mg/L)	Mg (mg/L)	Ba (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO4 (mg/L)	SiO2 (mg/L)	Sr (mg/L)	Br (mg/L)	Dissolved Solids (mg/L)
Mo-664	89-08-23	20.0	690	7.2	406	97	24	0.48	21	1.8	8.0	20	36	0.63	0.11	365
Mo-665	89-08-16	20.0	3010	- -	556	160	56	1.0	380	4.1	580	120	29	0.95	1.7	1570
Mo-666	88-11-10	18.0	655	7.3	323	81	14	0.30	17	2.4	9.4	12	34	0.43	0.05	224
Mo-685	89-07-05	22.0	560	6.0	271	- -	- -	- -	- -	- -	27	1.0	- -	- -	0.15	298
Mo-686	89-07-06	22.0	500	6.0	246	61	13	0.13	16	0.9	18	9.0	42	0.20	0.12	256
Mo-687	89-07-18	20.0	2850	7.4	619	190	59	0.38	320	3.7	450	240	28	1.1	1.3	1520
Mo-688	89-07-18	20.5	520	7.1	289	73	17	0.12	14	1.1	16	12	38	0.18	0.05	300
Mo-689	89-08-23	20.0	600	7.1	373	73	18	0.27	33	1.7	9.6	< 1.0	30	0.49	0.03	329
Mo-690	89-08-22	20.5	550	7.2	347	73	18	0.19	16	1.0	3.3	< 1.0	32	0.35	0.02	255
Mo-691	89-08-22	21.0	600	6.9	343	69	17	0.27	32	1.7	12	4.0	28	0.35	0.07	313
Mo-692	89-08-22	20.5	610	7.0	354	78	14	0.39	28	1.6	12	3.0	30	0.43	0.07	334
Mo-693	89-08-10	19.5	635	6.9	313	72	18	0.40	34	2.0	38	14	35	0.60	0.14	335
Mo-695	89-08-10	19.5	1060	- -	432	110	38	0.17	57	2.1	73	98	35	0.47	0.19	576
Mo-696	89-08-10	20.5	1360	7.2	484	130	54	0.13	87	2.8	88	190	32	0.49	0.22	712
Ch-1	89-10-25	18.5	1580	6.8	410	110	40	0.38	150	2.5	240	130	29	0.64	1.4	896
Ch-2	89-10-25	19.0	1610	7.0	422	110	40	0.28	160	2.2	220	160	30	0.57	0.49	907
Ch-3	89-10-25	19.0	1890	7.0	419	100	40	0.19	220	2.2	310	160	29	0.55	1.6	1070
Ch-4	89-10-25	19.0	1510	7.2	412	160	40	0.42	160	3.7	360	84	33	0.95	1.9	1060
Ch-5	89-10-24	19.0	4620	6.7	512	370	140	<0.1	380	5.2	1200	290	28	2.5	5.8	3030
Ch-6	89-10-24	19.5	5150	6.8	554	380	140	0.40	440	6.5	1300	320	26	2.6	6.5	3300
Ch-7	89-10-24	19.0	3540	7.0	468	240	74	0.40	350	4.7	810	200	28	1.5	4.4	2090
Ch-8	89-10-24	19.0	1900	7.0	432	170	34	0.40	82	3.8	160	190	22	0.56	0.45	865

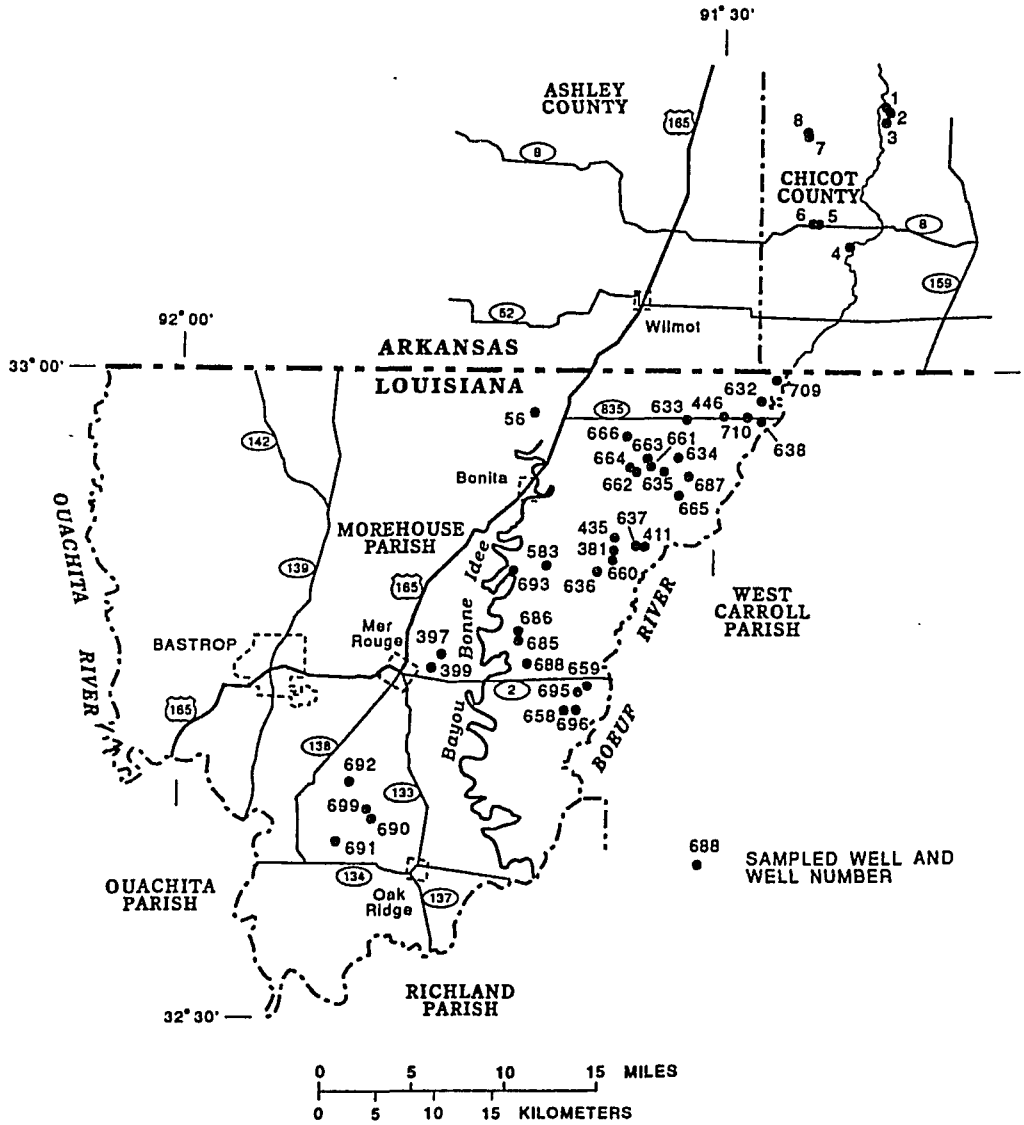


Figure 4.3 Location and identification numbers of sampled irrigation wells.

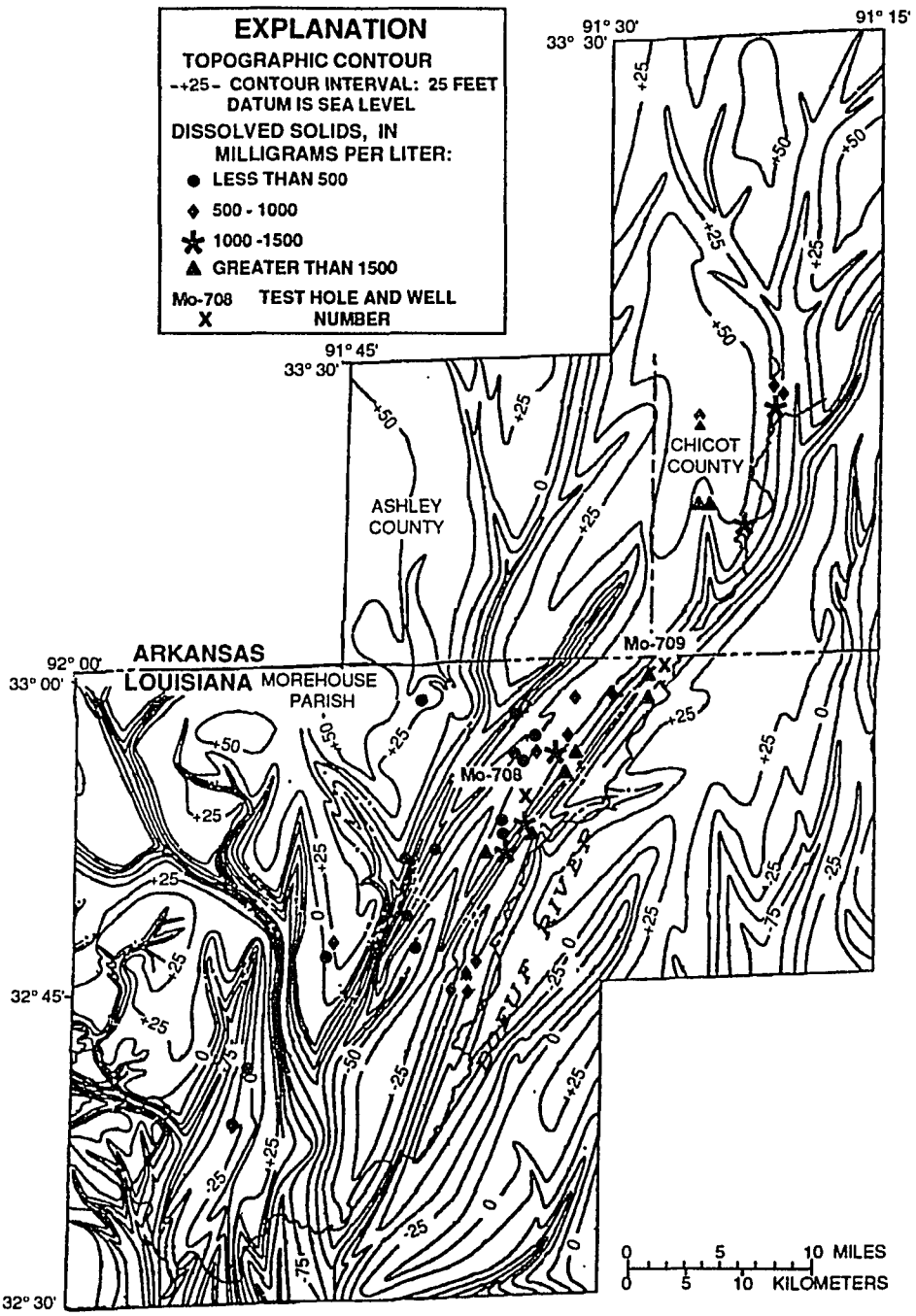


Figure 4.4 Dissolved solids concentrations in alluvial water shown on the mapped elevation of the unconformable contact between Mississippi River alluvial deposits and the underlying Cockfield formation. Paleotopograpy from Saucier (1967).

dissolved solids greater than approximately 800 mg/L fall within or near the mapped location of the easternmost fluvial channel. Brackish water occurs within, but is not limited to, the mapped location of this same fluvial channel in southern Chicot County.

The locations of two test holes drilled into the Cockfield aquifer through the easternmost fluvial channel (test hole Mo-709) and through an adjoining paleotopographic high on the Cockfield Formation (test hole Mo-708) are shown in figure 4.3. The trace of the electric logs (fig. 4.5) shows the total thickness of alluvial deposits to be approximately 40 m (130 ft) in test hole Mo-709 and approximately 27 m (90 ft) in test hole Mo-708. Measured induction resistivity (dashed line) is lower in test hole Mo-709 than in test hole Mo-708 for the total thickness of the Mississippi River Alluvial Aquifer. Measured normal resistivity (solid line) shows the same pattern with the exception of approximately the top 9 m (30 ft) of test hole Mo-709, where normal resistivity may have been affected by invasion of drilling fluid. In the absence of large changes in subsurface temperature or lithology, changes in the measured resistivity between two points in an aquifer should reflect changes in the dissolved-solids content of ground water. Driller's logs indicate lithologic changes between test holes Mo-708 and Mo-709 are limited to a greater fraction of coarse sand and small gravel in the lower approximately 12 m (40 ft) of test hole Mo-709 than is

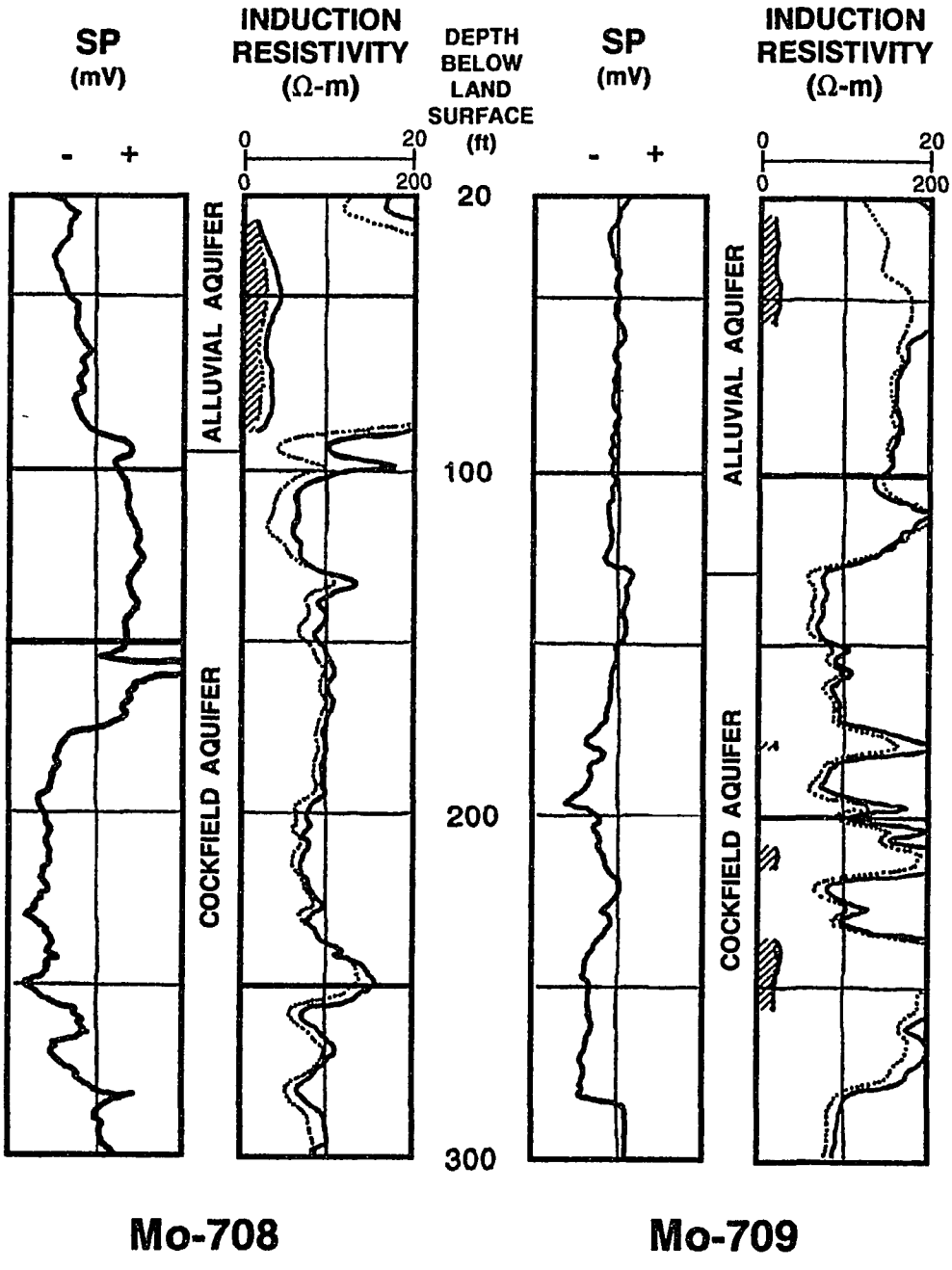


Figure 4.5 Trace of SP and induction resistivity logs in test holes Mo-708 and Mo-709.

present in test hole Mo-708. Thus, the lower resistivity measured in test hole Mo-709 indicates the presence of ground water which has greater concentrations of dissolved solids than in test hole Mo-708.

Paleotopographic Controls on the Distribution of Brackish Water

The trace of the induction resistivity log in test hole Mo-709 shows higher resistivities in the sandy interval of the Cockfield aquifer at approximately 44 to 50 m (145 to 165 ft) below sea level than in the overlying Alluvial Aquifer. This suggests the presence of water with lower concentrations of dissolved solids in the Cockfield aquifer than in the overlying Alluvial Aquifer. Wells Mo-709 and Mo-710 are located approximately 30 m (100 ft) apart at the site of test hole Mo-709 (fig. 4.3) and are screened in the Cockfield aquifer at approximately 47 to 53 m (155 to 175 ft) below sea level and in the Alluvial Aquifer at approximately 9 to 12 m (30 to 40 ft) below sea level, respectively.

The dissolved-solids concentration of a water sample from well Mo-709 (895 mg/L), compared to a water sample from well Mo-710 (1,800 mg/L), confirms that water in the Alluvial Aquifer within the easternmost fluvial channel contains a greater concentration of dissolved solids than water present in the underlying Cockfield aquifer. The presence of less saline water in the Cockfield aquifer

indicates that upward flow within the easternmost fluvial channel is not a source of brackish water in the Alluvial Aquifer.

Schincariol and Schwartz (1990) have experimentally shown that density contrasts created by differences in salinity of approximately 2,000 mg/L at constant temperature are sufficient to cause gravitational instability between two aqueous fluids. A representative sample of fresh alluvial water in eastern Morehouse Parish has a dissolved-solids concentration of approximately 200 mg/L, while a representative sample of brackish water in southern Chicot County has a dissolved-solids concentration of approximately 2,000 mg/L.

The easternmost fluvial channel in Morehouse Parish intersects a zone of brackish water in southern Chicot County. Because the density of brackish water is greater than that of freshwater, brackish water present in southern Chicot County could become trapped within the easternmost fluvial channel and flow southwestward into eastern Morehouse Parish.

Rate of Brackish Water Movement

Mississippi River alluvial water in eastern Morehouse Parish having concentrations of dissolved solids greater than approximately 1,000 mg/L apparently does not presently extend south of Louisiana Highway 2. The occurrence of

brackish alluvial water in northeastern Morehouse Parish was reported by Sanford (1973). Until the present study, the areal distribution of salinity within the Alluvial Aquifer of eastern Morehouse Parish had not been mapped in detail. Insufficient data therefore exist to construct a detailed history of movement of brackish water in eastern Morehouse Parish.

Because brackish water appears to be confined within the easternmost fluvial channel, future lateral spreading is unlikely. Ignoring the effects of hydrodynamic dispersion, brackish water in the easternmost fluvial channel is calculated to be moving southwestward at approximately 9.3 m/yr (30 ft/yr). Details of this calculation are given in Appendix V. This calculated rate of movement is an approximation only. It does indicate, however, that the actual rate of movement is occurring on a human time scale.

Composition of Fresh and Brackish Water

Figure 4.6 shows the relative abundance of Na, Ca plus Mg, Cl, and HCO_3 as a function of the concentration of dissolved solids in alluvial water. The relative abundance of Cl systematically increases while the relative abundance of HCO_3 systematically decreases with increasing concentration of dissolved solids. This relation would be expected on mixing of water having a relatively high concentration of dissolved solids in which Cl is the

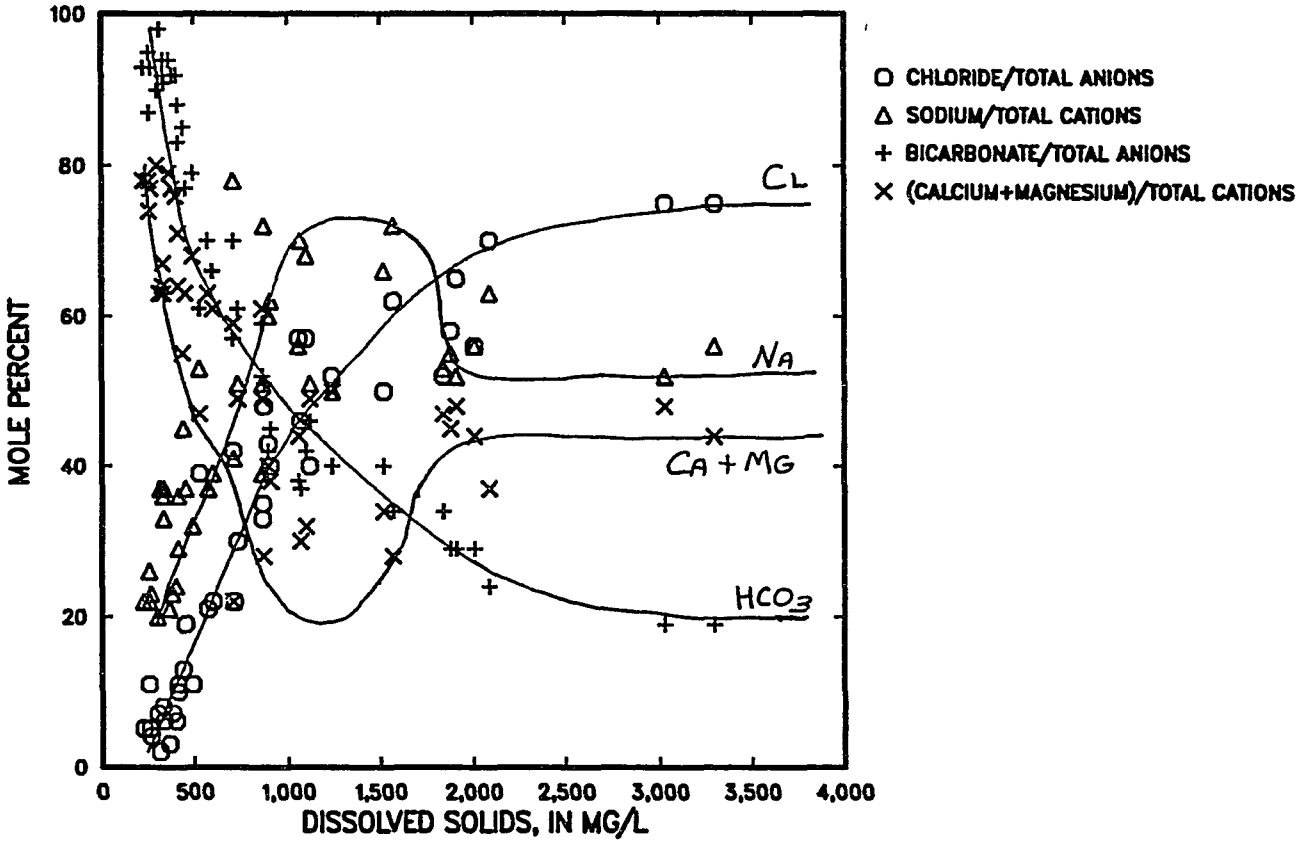


Figure 4.6 Relative abundances of Na, Ca plus Mg, Cl, and HCO_3 as a function of dissolved solids concentrations in alluvial water.

dominant anion, with water having a relatively low concentration of dissolved solids in which HCO_3 is the dominant anion. Fresh Ca-HCO_3 type end-member water and more saline end-member water having elevated concentrations of Cl are known to exist in the Alluvial Aquifer of the Morehouse Parish study area (Sanford, 1973).

The relative abundance of Na systematically increases and the relative abundance of Ca plus Mg systematically decreases with increasing concentrations of dissolved solids up to a dissolved-solids concentration of approximately 1,000 mg/L. This relation would be expected on mixing of water having a relatively high concentration of dissolved solids in which Na is the dominant cation, with water having a relatively low concentration of dissolved solids in which Ca plus Mg represent the dominant cationic species.

Cl is the dominant anion in all sampled alluvial water with dissolved-solids concentrations greater than approximately 1,000 mg/L. Sampled alluvial water with dissolved-solids concentrations ranging from approximately 1,000 to 2,000 mg/L contain Na as the dominant cationic species. Sampled alluvial water with dissolved-solids concentrations greater than approximately 2,000 mg/L contain Na and Ca plus Mg in approximately equal amounts. The behavior of Na and Ca plus Mg in the range of dissolved solids between approximately 1,000 to 2,000 mg/L suggests that a process other than simple mixing is taking place.

These data could be explained by cation exchange of Ca or Mg in solution for Na on sediment-hosted exchange sites.

Because Br and Cl are assumed to behave conservatively in this ground-water system, their geochemistry can be interpreted in terms of mixing curves. Concentrations of Br and Cl from samples of alluvial water plotted against one another in figure 4.7. A modern seawater mixing curve is also shown in figure 4.7 for reference. Data from the Alluvial Aquifer fall along two distinct trends. A best-fit line has been drawn through each of the data trends using the least-squares linear regression technique. Each separate data trend in figure 4.7 represents Br and Cl concentrations produced by mixing of fresh alluvial water with ground waters having higher concentrations of Br and Cl. Because the compositions of end members lie on or along an extension of a given mixing curve, the presence of two distinct trends in the data indicates the presence of two more-saline end members with distinct Br/Cl ratios.

Figure 4.8 shows the relation between the Br/Cl ratio as a function of the concentration of Cl in alluvial water samples. For reference, mixing curves showing calculated Br/Cl ratios and Cl concentrations on mixing of modern seawater with fresh alluvial water are also shown in figure 4.8. The compositions used for fresh alluvial end members in constructing the modern-seawater mixing curves are those which appear at the low-Cl end of the mixing curves near the dependent axis.

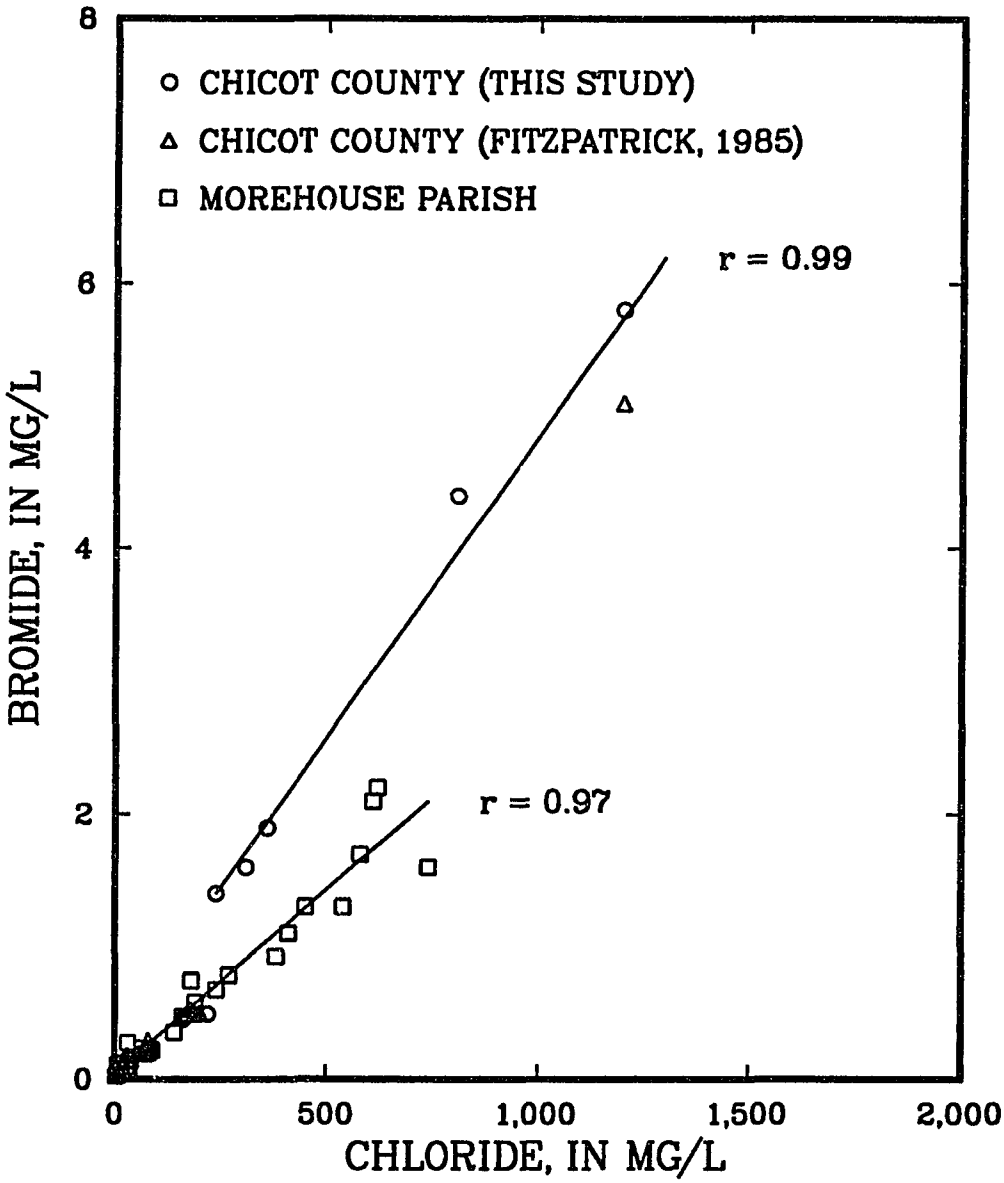


Figure 4.7 Br concentrations as a function of Cl concentrations in alluvial water.

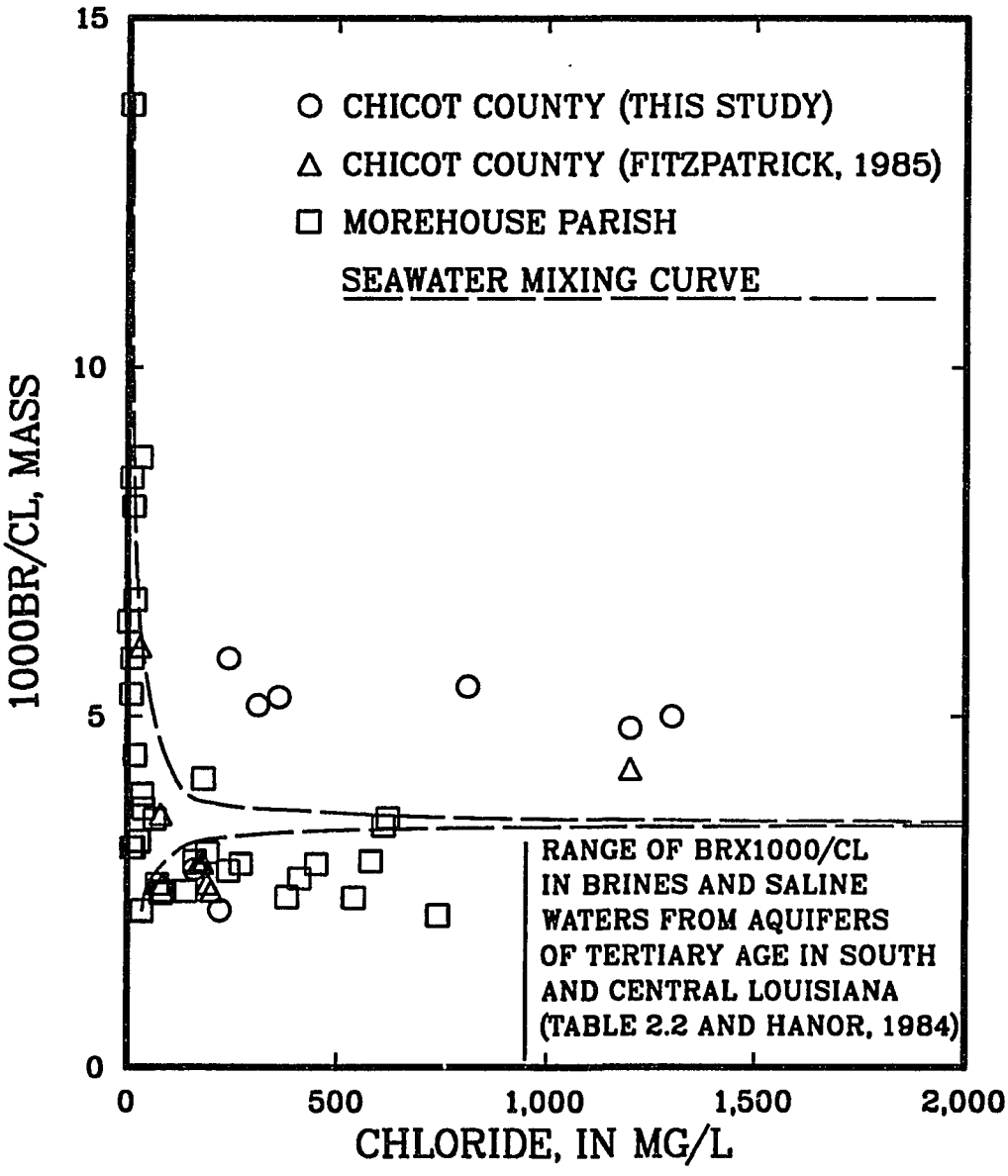


Figure 4.8 Br/Cl ratio as a function of Cl concentrations in alluvial water.

In addition to providing a frame of reference, the modern-seawater mixing curve in figure 4.8 shows the rapid convergence of Br/Cl ratio in a mixture of dilute and more saline end members toward the value in the more saline end member. Inspection of figure 4.8 shows that most of the data points representing Cl concentrations of approximately 50 mg/L or greater fall into two clearly defined groups. One of these groups of data points represents alluvial water with Br/Cl ratios greater than that of modern seawater, while the other group of data points represents alluvial water with Br/Cl ratios less than that of modern seawater. The Br/Cl ratio of alluvial water where it is less than that of modern seawater overlaps that of brines and saline waters from Tertiary aquifers in south (Hanor, 1984; 1987, p. 81-82) and central (table 2.2) Louisiana.

While neither group of data points is completely confined to a specific geographic location within the study area, most of the data points representing alluvial water having Br/Cl ratios greater than that of modern seawater correspond to sampling locations in southern Chicot County. Conversely, most of the data points representing alluvial water having Br/Cl ratios less than that of modern seawater correspond to sampling locations in Morehouse Parish. The scatter observed in some data points in figures 4.7 and 4.8 may reflect heterogenous mixing of end members having differing Br/Cl ratios.

The effects of two geochemically distinct more-saline end-members on the composition of brackish alluvial water are exemplified by samples from wells Ch-5, Ch-6, Mo-665, and Mo-687. Wells Ch-5 and Ch-6 are located within the area of anomalous salinity in southern Chicot County, Arkansas. These wells produced alluvial water in with Br/Cl ratios of approximately 4.9×10^{-3} and 5.0×10^{-3}, respectively, clearly above the value of 3.46×10^{-3} for modern seawater (Drever, 1982). Wells Mo-665 and Mo-687 are located in the easternmost fluvial channel near the Louisiana-Arkansas State line. These wells produced alluvial water in which Br/Cl ratios were approximately 2.9×10^{-3} in each well, clearly below the value for modern seawater. These distinctly different Br/Cl ratios indicates that two geochemically distinct sources of salinity are present in the Alluvial Aquifer. In order to understand the origin of these geochemically distinct sources of brackish water, the regional geochemistry of deep subsurface ground waters and regional ground-water flow patterns in both deep and shallow aquifers must be considered.

Origins of Brackish Water

Tertiary Aquifers

A part of the precipitation falling on the highlands to the west of the Mississippi River Alluvial Valley travels

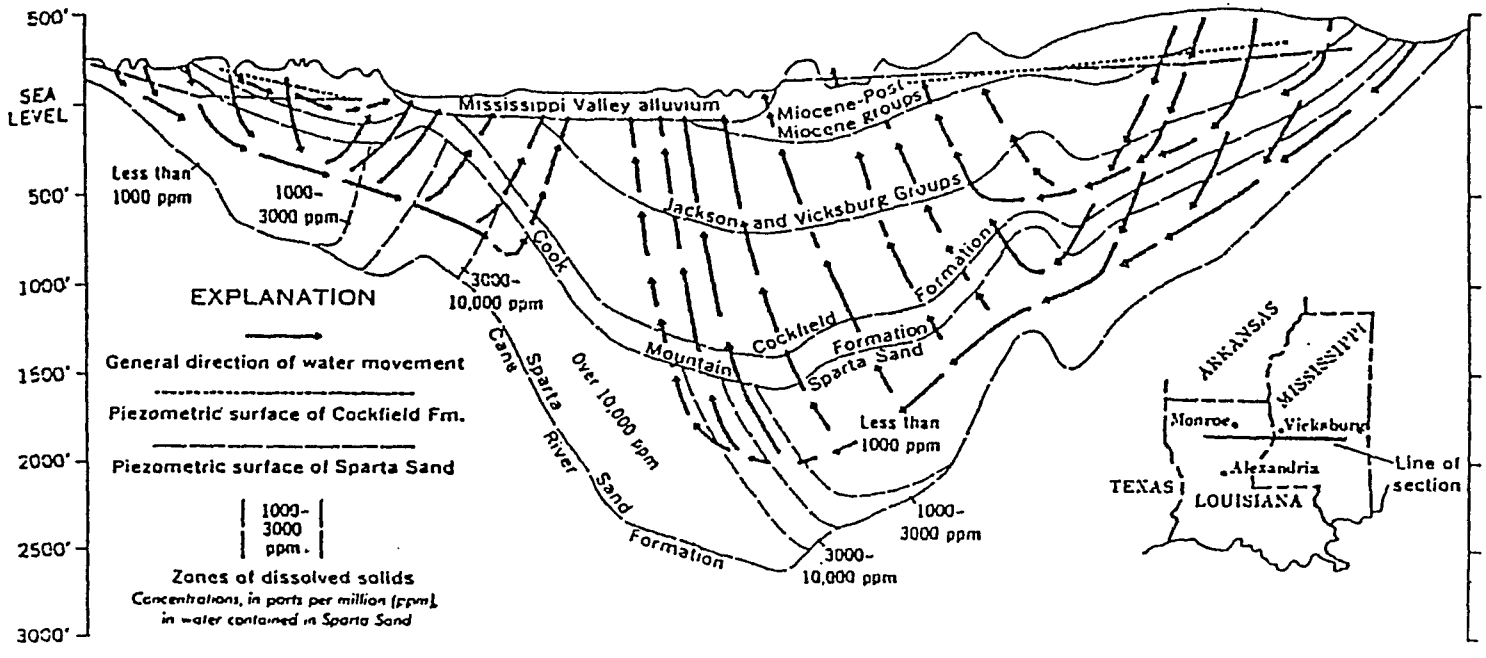


Figure 4.9 Regional ground-water flow pattern in the Mississippi River Alluvial Valley (Payne, 1968).

downward and eastward into Tertiary aquifers (the Sparta aquifer or perhaps deeper into the Wilcox aquifer) before circulating upward and entering the Alluvial Aquifer from below (Payne, 1968) (fig. 4.9). Deeply circulating ground water along this flow pattern is brought into contact with brackish to saline water in Tertiary aquifers having dissolved-solids concentrations ranging from 3,000 to greater than 10,000 mg/L. A similar circulation pattern exists on the eastern side of the Mississippi River alluvial valley, also bringing deeply circulating ground water into contact with brackish to saline water in Tertiary aquifers (Payne, 1968). Upward circulating ground water would then contain a greater concentration of dissolved solids, derived from mixing with more saline ground water at depth, than is present in fresh alluvial water.

Upward flow of brackish water due to the presence of a pattern of ground-water circulation similar to that shown in figure 4.9 along the Mississippi River Alluvial Valley could account for the zone of dissolved-solids elevated salinity in the Alluvial Aquifer (figure 1.8).

Hanor (1984; 1987, p. 81-82) and Bennett and Hanor (1987) have proposed that brines and waters within Tertiary aquifers in south Louisiana, which are Na-Cl type waters with Br/Cl ratios less than that of modern seawater, are created by subsurface dissolution of halite. The flow model of Williamson and others (1990) indicates that lateral flow into the Sparta aquifer of northeastern Louisiana comes form

the southeast (fig. 4.10). This lateral flow pattern would bring water from the area of the Mississippi Salt Dome Basin into the Sparta aquifer. Vertical flow in northeastern Louisiana is upward from the upper unit of the Wilcox aquifer into the Sparta aquifer. Regardless of their exact origin, brackish to saline water in Tertiary aquifers originating from dissolution of halite should have Br/Cl ratios less than that of modern seawater. A pattern of upward circulation bringing these waters into the Alluvial Aquifer would provide the more saline end member required to produce brackish alluvial water with Br/Cl ratios less than that of modern seawater.

The Smackover Formation

Brackish alluvial waters having Br/Cl ratios greater than that of modern seawater require a saline source which also has Br/Cl ratios greater than that of modern seawater. The Jurassic Smackover Formation is present at 1675 to 1975 m (5,500 to 6,500 ft) below sea level in the study area (fig. 4.2). Smackover Formation brines in southwestern Arkansas have Br/Cl ratios which are among the highest reported in the literature for natural waters (Collins, 1974; Carpenter and Trout, 1978; Moldovanyi and Walter, 1992). The geochemistry of Smackover brines has been discussed in Chapter I. No attempt will be made here to support or discredit any theories on the formation of high

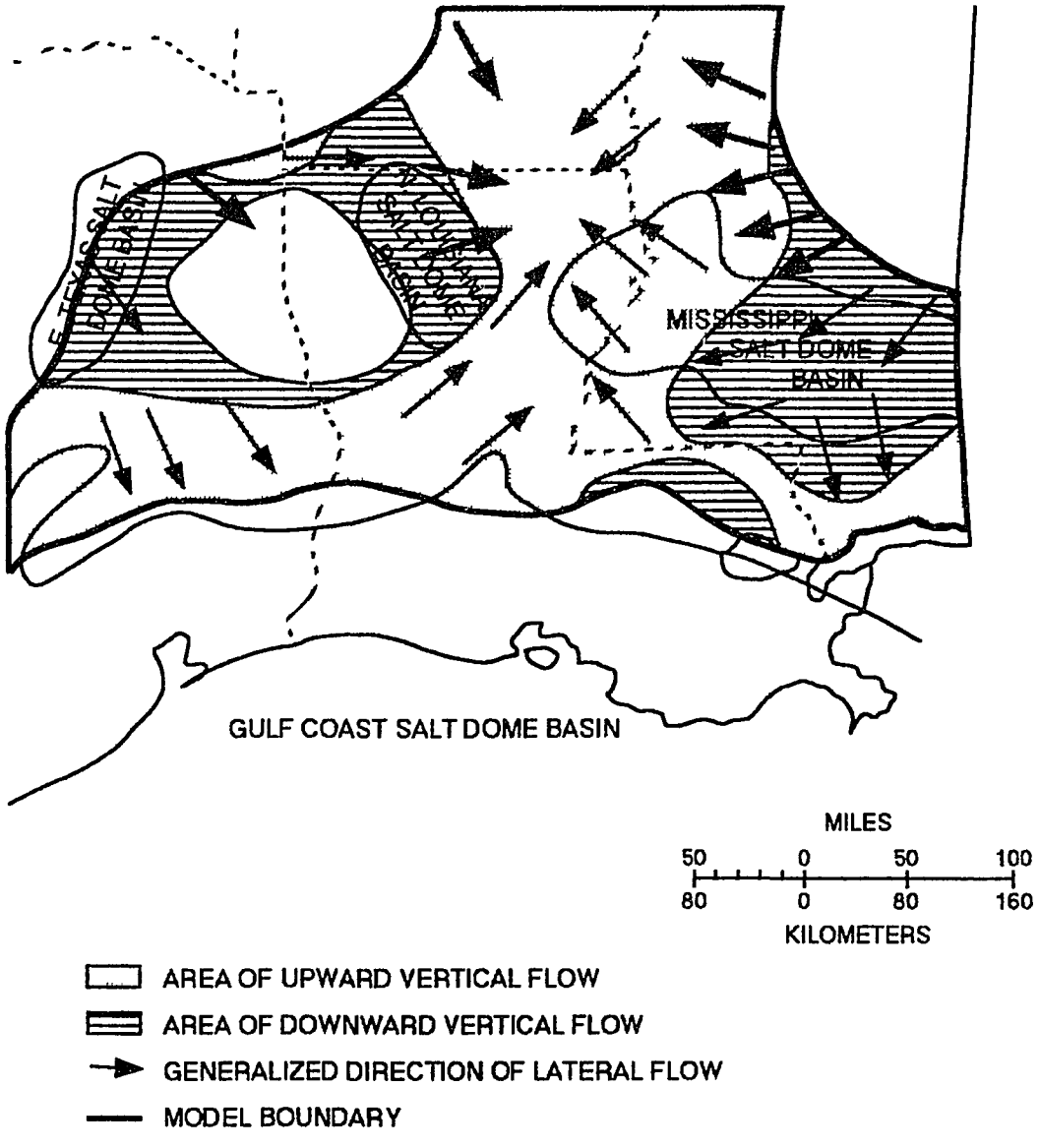


Figure 4.10 Lateral ground-water flow directions in the Sparta Aquifer. Flow directions modified from Williamson and others (1990). Base map modified from Holcomb (1971).

Br/Cl ratio Smackover brines or to propose new ones. However, the high Br/Cl ratio of Smackover brines will be used as a tracer of subsurface fluid flow.

High Br/Cl-ratio brines within the Smackover Formation are associated with an east-west trending, trough-shaped structure approximately 200 km long and 40 km wide (125 miles long and 25 miles wide) (Carpenter, 1984). High Br/Cl-ratio brines within the Smackover Formation have not been confirmed to occur in Chicot County possibly because of the lack of oil and gas development in the area. It is not unreasonable to assume, however, that high Br/Cl-ratio brines which occur along an east-west trend in southwestern Arkansas could extend into Chicot County. As such, high Br/Cl-ratio brines from within the Smackover Formation represent a possible end member in a mixing scheme that could produce brackish alluvial water with Br/Cl ratios greater than that of modern seawater.

Hydrogeochemistry of Brackish Water

Figure 4.11 shows average concentration of Br and Cl in selected bodies of ground water from south and central Louisiana northward to southeastern Arkansas. The average composition of fresh to brackish alluvial water from the Morehouse Parish study area having Br/Cl ratios less than that of modern seawater (point B) falls near a mixing line between the average composition of fresh alluvial water from

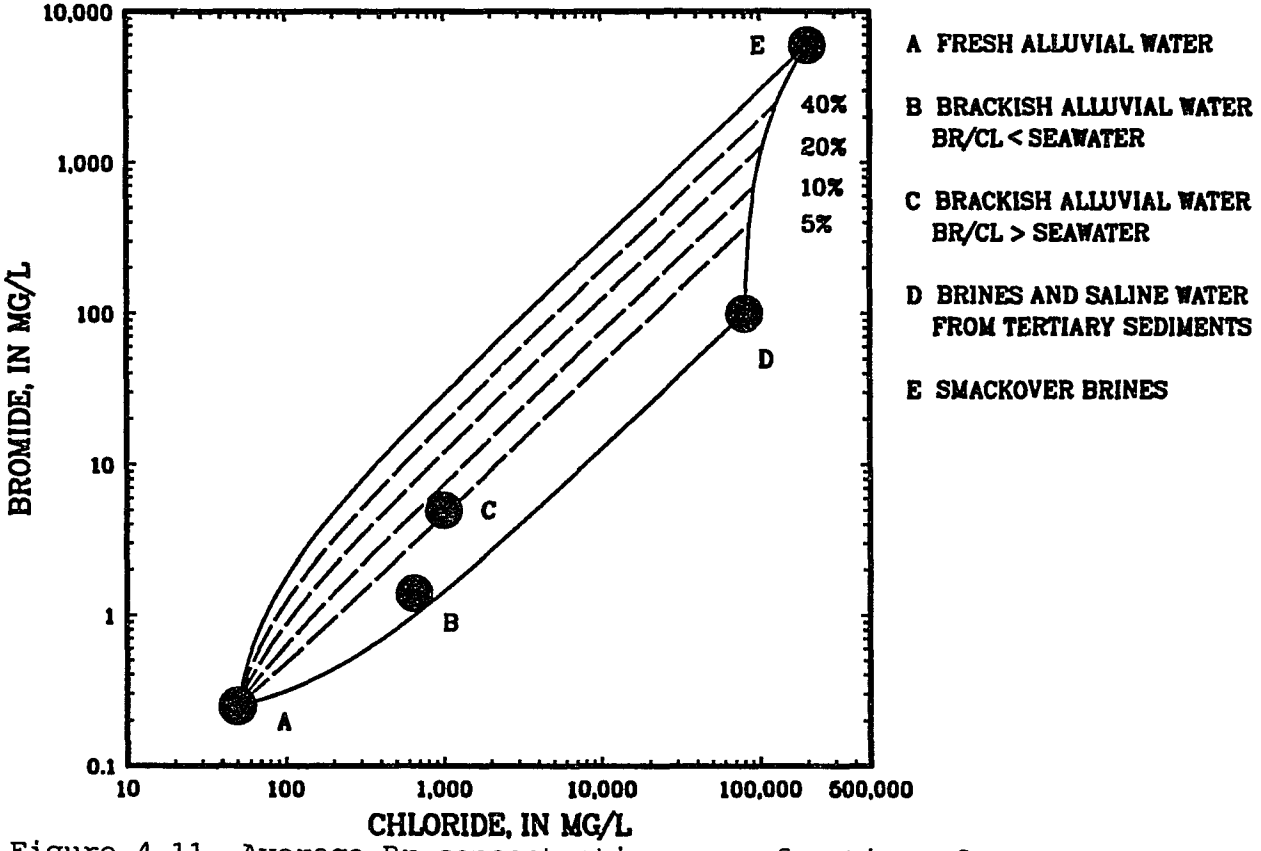


Figure 4.11 Average Br concentration as a function of average Cl concentration in selected bodies of ground water in northern and central Louisiana and southern Arkansas. Composition 'D' from Hanor (1984) and table 2.2. Composition 'E' from Collins (1974) and Carpenter and Trout (1978).

the Morehouse Parish study area (point A) and the average composition of brines and saline waters from Tertiary aquifers in south and central Louisiana (point D). The relation of points A, B, and D indicate that fresh to brackish water in the Alluvial Aquifer having Br/Cl ratios less than that of modern seawater could be formed by a binary mixture of fresh alluvial waters and brines or saline waters originating from dissolution of halite.

The average composition of fresh to brackish alluvial water with Br/Cl ratios greater than that of modern seawater is represented by point C in figure 4.11. The average composition of high Br/Cl-ratio brines from within the Smackover Formation is represented by point E in figure 4.11. Because point C does not lie on a mixing line between the average composition of fresh alluvial water (point A) and either known more saline end member (points D and E), the composition of fresh to brackish alluvial water with Br/Cl ratios greater than that of modern seawater cannot be explained as a binary mixture of fresh alluvial water with either known more saline end member.

Dashed lines in figure 4.11 represent compositions produced by mixing of fresh alluvial water with more-saline compositions intermediate between Smackover brines and brines and saline water from aquifers of Tertiary age. The composition of brackish alluvial water having Br/Cl ratios greater than that of modern seawater falls near a mixing line representing a more-saline end-member composition

characteristic of approximately 5% Smackover brine and 95% brine or saline water from aquifers of Tertiary age.

Based on the geochemistry of Br and Cl, two geochemically distinct sources of brackish water can be shown to exist in the Alluvial Aquifer. Fresh of brackish alluvial water with Br/Cl ratios less than that of modern seawater are produced by mixing of freshwater circulating to altitude of over 2,500 feet below sea level with brines or saline ground waters in aquifers of Tertiary age, such as the Sparta aquifer. Circulating ground water returns toward the surface and flows upward through the base of the Alluvial Aquifer as a part of the regional ground-water flow pattern.

Fresh to brackish alluvial water with Br/Cl ratios greater than that of modern seawater could be derived from a mixture of approximately 5% Smackover brine and 95% brine or saline water from aquifers of Tertiary age. In order for Smackover brines to play a role in the geochemistry of alluvial water, a mechanism must exist for transporting these brines or ground waters derived from them, through the base of the Alluvial Aquifer.

The areal distribution of maximum Cl concentrations in water from the Alluvial Aquifer of southern Chicot County occurs along a roughly north-south trend in an area approximately 27 km long and 5 km wide (17 miles long and 3 miles wide) (Fitzpatrick, 1985) and coincides with the area of anomalous salinity mapped by Boswell and others (1968)

(figs. 1.8 and 4.12). This areal distribution of maximum Cl concentrations is not consistent with a point source of contamination, such as an abandoned oil well or test hole. Fitzpatrick (1985) has suggested that brackish water may migrate by upward flow along a fault or through a thin or missing area of the regional confining layer (Jackson Formation) which underlies the Cockfield aquifer in southern Arkansas. Less restricted upward flow in an area where the Jackson Formation is thin or missing could explain a localized increase in salinity. However, upward flow in an area where the Jackson Formation is thin or missing does not account for the geochemistry of Br and Cl observed within the area of anomalous salinity.

Broom and others (1984) reported locally occurring brackish water in the upper part of the Sparta aquifer to the west of the study area in Union County, Arkansas in association with graben-bounding faults. The depth of fault penetration was not reported by Broom and others (1984). The presence of graben-bounding faults in proximity to the area of localized maximum salinity suggests that these faults may act as conduits along which dissolved solids migrate from depth. The area of anomalous salinity as mapped by Boswell and others (1968) and Fitzpatrick (1985) coincides with the intersection of two regional wrench faults mapped by Zimmerman (1992) in southern Chicot County, Arkansas (fig. 4.12). The northeast-southwest trending wrench fault deforms

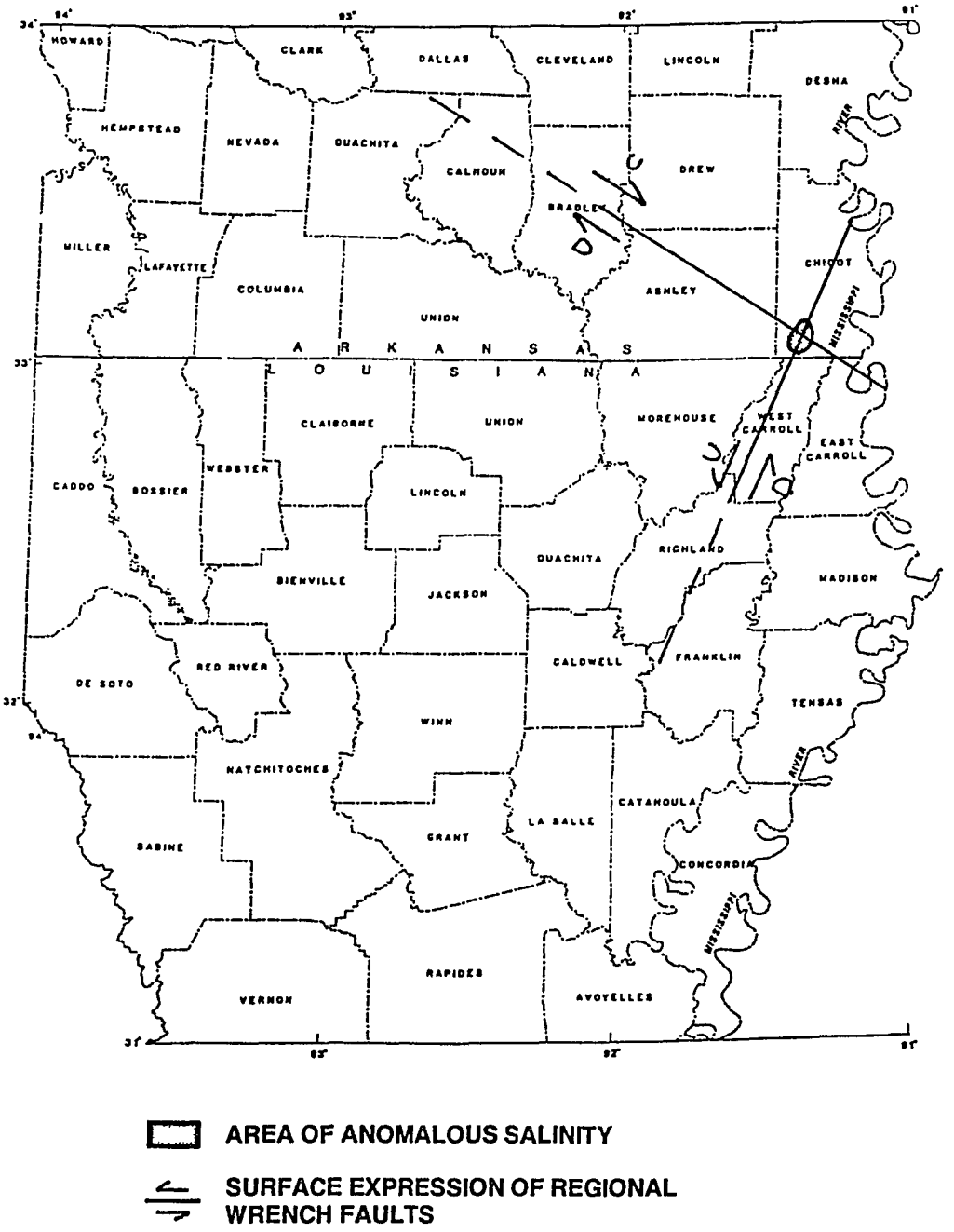


Figure 4.12 Area of anomalous salinity (Boswell and others, 1968) and surface expression of regional wrench faults (Zimmerman, 1992).

sediments as old as Jurassic and may have been active through Holocene time (Zimmerman, 1992).

Upward movement of dissolved solids, derived at least in part from Smackover brines, near the intersection of the wrench faults shown in figure 4.12 would provide the Br-enriched water required to explain the observed Br/Cl ratios of brackish water in the area of anomalous salinity. In addition, an increase in hydraulic conductivity at the intersection of these wrench faults could account for the location of the area of anomalous salinity. Br/Cl ratios of brackish water in the area of anomalous salinity indicate that the Smackover-derived component is relatively small. Any component of Smackover-derived water flowing away from the intersection of the wrench faults would be further mixed with waters having Br/Cl ratios less than that of modern seawater derived from the regional ground water flow pattern. This likely accounts for the lack of Smackover signature in brackish waters of the easternmost fluvial channel in Morehouse Parish.

CHAPTER SUMMARY

The distribution of brackish alluvial water in eastern Morehouse Parish, Louisiana is controlled by the paleotopography of the unconformable contact between Pleistocene Mississippi River alluvial deposits and Tertiary sediments of the Cockfield Formation. Brackish water moves

into the Alluvial Aquifer in southern Chicot County by upward flow as a part of the regional ground-water flow pattern. Because the density of brackish water in southern Chicot County is greater than that of the surrounding fresh ground water, the brackish water becomes trapped within a northeast-southwest trending fluvial channel eroded into Cockfield sediments and flows along the fluvial channel to the southwest into Morehouse Parish. The rate of advancement of the brackish-water front in the fluvial channel was calculated to be approximately 10 m per year. This rate of advancement of the brackish-water front does not take the effects of dispersion or retardation into account.

Alluvial water with concentrations of Cl greater than approximately 50 mg/L can be divided into two groups based on the Br/Cl ratio. One group has a Br/Cl ratio less than that of modern seawater while the other group has a Br/Cl ratio greater than that of modern seawater.

The geochemistry of fresh to brackish alluvial water with Br/Cl ratios less than that of modern seawater can be explained as a binary mixture of fresh alluvial water with more saline water derived from dissolution of halite. Halite dissolution producing these waters is likely occurring in the Mississippi Salt Dome Basin. The geochemistry of fresh to brackish alluvial water with Br/Cl ratios greater than that of modern seawater can be explained as a ternary mixture of fresh alluvial water, more-saline water derived

from dissolution of halite, and more-saline water derived from the Smackover Formation of Jurassic age.

Brackish water with Br/Cl ratios less than that of modern seawater is introduced into the Alluvial Aquifer of southern Chicot County by upward flow as part of the natural ground-water flow system. Fresh to brackish alluvial water with Br/Cl ratios greater than that of modern seawater can be explained by upward movement of dissolved solids from the Smackover Formation along the intersection of two wrench faults, at least one of which extend from the Smackover Formation to or near the base of the Alluvial Aquifer, followed by mixing with fresh alluvial water and fresh to brackish alluvial water with Br/Cl ratios less than that of modern seawater. The Smackover Formation contributes approximately 5% of the Br and Cl present in brackish alluvial water in the area of anomalous salinity.

CHAPTER V

CONCLUSIONS

BRACKISH WATER IN THE ALLUVIAL AQUIFER AND JASPER AQUIFER SYSTEM IN CONCORDIA PARISH, LOUISIANA

Samples of water from irrigation and monitor wells screened within the Alluvial Aquifer and the uppermost part of the Jasper aquifer system show the presence of brackish water in proximity to plugged and abandoned oil wells and test holes. Brackish water in the Alluvial Aquifer and uppermost part of the Jasper aquifer system is interpreted to be a mixture of fresh water and saline waters or brines from depth. Saline waters and brines from the Wilcox aquifer at depths of 1,750 to 2,100 m (5,800 to 6,800 ft) below sea level have Br and Cl geochemistry and $^{87}Sr/^{86}Sr$ values consistent with those required to generate brackish water in the Alluvial Aquifer and the uppermost part of the Jasper aquifer system by mixing with fresh ground water. It is concluded here that plugged and abandoned oil wells and test holes which penetrate to depths of 1,750 to 2,100 m (5,800 to 6,800 ft) below sea level provide avenues of movement for saline waters and brines in the Wilcox aquifer into the Alluvial Aquifer and the uppermost part of the Jasper aquifer system.

BRINES AND SALINE WATERS IN THE WILCOX AQUIFER OF EASTERN CENTRAL LOUISIANA

Brines and saline waters in the Wilcox aquifer of eastern central Louisiana are Na-Cl type waters with dissolved solids concentrations ranging from 83 to 150 g/L. Concentrations of dissolved solids generally increase with depth. Concentrations of all determined species increase with increasing concentrations of dissolved solids with the exceptions of alkalinity, Mg, and Sr. Alkalinity decreases rapidly with increasing concentrations of dissolved solids up to approximately 110 g/L. Concentrations of dissolved Mg decrease with increasing concentrations of dissolved solids while Sr shows little or no change. Values of the Br/Cl ratio fall between approximately 0.85×10^{-3} and 1.1×10^{-3}. Values of $\delta^{18}O$ and δD are approximately -1 o/oo and -13 to -15 o/oo, respectively, and show no change with increasing concentrations of analytical dissolved solids. These values of $\delta^{18}O$ and δD represent shifts of approximately +3 o/oo and +6 o/oo, respectively, from reported values of Gulf Coast meteoric water.

The rapid decrease in alkalinity with increasing concentrations of dissolved solids can be explained by precipitation of calcite on mixing of brines and saline water in the upper and middle units of the Wilcox aquifer where the Big Shale is absent. The limited range of concentration of dissolved Sr suggests that rock buffering may control Sr concentrations in solution. Precipitation of

a $(Ca,Mg,Sr)CO_3$ solid solution may place an upper limit on the concentration of Sr in aqueous solution. The apparent decrease in dissolved Mg concentrations with increasing concentrations of dissolved solids may reflect increased partitioning of Mg into a $(Ca,Mg,Sr)CO_3$ solid solution with increasing temperature.

The observed +3 o/oo shift in $\delta^{18}O$ over the entire range of dissolved solids concentrations may also reflect the effects of rock buffering. The observed +6 o/oo shift in δD values may be explained by the presence of meteoric water heavier than values previously reported for the Gulf Coast.

The Gulf Coast regional average for diapiric salt is approximately 50 mg Br/kg halite. Recrystallization of halite has been proposed as a mechanism for producing the observed Br content of Gulf Coast brines and saline waters. Brines and saline waters in the Wilcox aquifer, however, have Br/Cl ratios expected on formation from recrystallizing salt containing approximately 15 mg Br/kg halite. This indicates that the Br/Cl ratios of Wilcox brines and saline waters have been determined, in part, by dissolution rather than recrystallization of halite.

The relationship between $^{87}Sr/^{86}Sr$ and 1/Cl is consistent with a heterogenous mixture of a more-saline end-member having $^{87}Sr/^{86}Sr$ values more radiogenic than mid-Jurassic seawater and a less-saline end-member having $^{87}Sr/^{86}Sr$ values similar to mid-Jurassic seawater. Regional patterns of ground-water flow in the Wilcox aquifer allow

more radiogenic Sr to be derived from the Gulf Coast Salt Dome Basin and less radiogenic Sr to be derived from the North Louisiana Salt Dome Basin.

Distributions of salinity and density as well as geochemical evidence indicates that vertical mixing between the upper and middle units of the Wilcox aquifer is greatly enhanced in the absence of the Big Shale. The Big Shale, where present, may act as an aquitard between the upper and middle units of the Wilcox aquifer.

BRACKISH WATER IN THE ALLUVIAL AQUIFER OF MOREHOUSE PARISH, LOUISIANA AND SOUTHERN CHICOT COUNTY, ARKANSAS

The location of brackish alluvial water in eastern Morehouse Parish, Louisiana is controlled by the paleotopography of the unconformable contact between Pleistocene Mississippi River alluvial deposits and Tertiary sediments of the Cockfield Formation. Brackish water moves into the Alluvial Aquifer in southern Chicot County by upward flow as a part of the regional ground-water flow pattern. Because the density of brackish water in southern Chicot County is greater than that of the surrounding fresh ground water, the brackish water becomes trapped within a northeast-southwest trending fluvial channel eroded into Cockfield sediments and flows along the fluvial channel to the southwest into Morehouse Parish. The rate of advancement of brackish water in the fluvial channel is calculated to be approximately 10 m per year. This rate of advancement of the

brackish-water front does not take the effects of dispersion or retardation into account.

Alluvial waters with concentrations of Cl greater than approximately 50 mg/L can be divided into two groups on the basis of Br/Cl ratios. One group has a Br/Cl ratio less than that of modern seawater while the other group has a Br/Cl ratio greater than that of modern seawater.

The geochemistry of fresh to brackish alluvial water with Br/Cl ratios less than that of modern seawater can be explained as a binary mixture of fresh alluvial water with more saline water derived from dissolution of halite. Regional ground-water flow suggests that halite dissolution producing these waters is likely occurring in the Mississippi Salt Dome Basin. The geochemistry of fresh to brackish alluvial water with Br/Cl ratios greater than that of modern seawater can be explained as a ternary mixture of fresh alluvial water, more-saline water derived from dissolution of halite, and more-saline water derived from the Smackover Formation of Jurassic age.

Brackish water with Br/Cl ratios less than that of modern seawater is introduced into the Alluvial Aquifer of southern Chicot County by upward flow as part of the natural ground-water flow system. Fresh to brackish alluvial water with Br/Cl ratios greater than that of modern seawater can be explained by upward movement of dissolved solids from the Smackover Formation at the intersection of two wrench faults, at least one of which extends from the Smackover

Formation to or near the base of the Alluvial Aquifer, followed by mixing with fresh alluvial water and fresh to brackish alluvial water with Br/Cl ratios less than that of modern seawater. The Smackover Formation contributes approximately five percent of the Br and Cl present in brackish alluvial water in the area of anomalous salinity.

SIGNIFICANCE OF THIS STUDY

Tracing of solute sources in areas of aquifer contamination can have important environmental and legal ramifications. The combined use of Br, Cl, and Sr isotopes has been shown to be a relatively straightforward method of solute source determination in the case of oilfield water contamination of an otherwise freshwater aquifer.

Prior knowledge of the composition of brines and saline waters in the Wilcox aquifer of eastern central Louisiana was limited to data reported by Collins (1970). Funayama (1990) completed a large-scale investigation of subsurface salinity, including the Wilcox aquifer of eastern central Louisiana, and postulated long-distance transport of dissolved salt. Hanor and Sassen (1990) also postulated long-distance transport of solutes in the Wilcox aquifer. The work presented here confirms the contribution of halite dissolution as a major contributing factor to salinity in Wilcox brines. Sr-isotope data, interpreted within the framework of regional ground-water flow patterns, indicates

that Wilcox brines in eastern central Louisiana derive solutes form sources as remote as the Gulf Coast and the North Louisiana Salt Dome Basins. In addition, water-rock equilibria appear to play a major role in controlling the abundances of Sr, Mg, and ^{18}O in brines and saline water of the Wilcox aquifer.

Prior to this work, the understanding of origins of brackish water in the Alluvial Aquifer of northern Louisiana and southern Arkansas was limited to the studies of Whitfield (1975) and Fitzpatrick (1985). Brackish water was thought to be derived from underlying aquifers by a poorly understood mechanism. Geochemical data collected in this study and interpreted in the light of work by Payne (1968) and Williamson and others (1990) shows that brackish water in much of the Alluvial Aquifer of northern Louisiana and extreme southeastern Arkansas is a mixture of fresh alluvial water and saline water present in Tertiary aquifers which has been derived from dissolution of halite. Brackish to saline water is brought into the Alluvial Aquifer by a topographically-driven regional ground-water flow pattern. Other regional flow patterns suggest that halite dissolution contributing to the salinity of saline waters in Tertiary aquifers is occurring in the Mississippi Salt Dome Basin. Future work on the isotopes of Sr in brackish to saline waters in northern Louisiana and southern Arkansas could verify this proposed source of salinity.

The relationship between faulting and localized areas of elevated salinity in shallow aquifers was recognized by Broom and others (1984). The recent work of Zimmerman (1992) indicates that wrench faulting in southeastern Arkansas has deformed Tertiary (and possibly Quaternary) through Jurassic sediments. The geochemistry of brackish water in the Alluvial Aquifer, associated with the intersection of two regional wrench faults, shows the influence of Smackover brines. This establishes faulting in addition to regional flow as a mechanism for introduction of water having elevated salinities, possibly from great depth, into shallow aquifers. The presence of plugged and abandoned oils well has also been shown to contribute to localized areas of elevated salinity in shallow aquifers.

Once waters with greater than ambient density are introduced into the Alluvial Aquifer, the paleotopography of the unconformable contact between alluvial deposits and the underlying Cockfield Formation exerts a controlling influence on their rate and direction of movement. An analytical expression for the rate of movement for denser than water liquids in deep confined aquifers was developed by Dortgarten and Tsang (1991). In this work, an analytical expression has been developed describing the rate of movement of a denser than ambient liquid (brackish water) along the base of a sloping unconfined aquifer.

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APPENDIX A

GEOCHEMICAL TRACERS IN GROUND WATER

Variations in the ratios of major chemical constituents including Ca/Cl, Mg/Cl, SO_4/Cl (Leonard, 1964; Leonard and Kleinschmidt, 1976), and Na/Cl (Magaritz and others, 1981) have been used in identification of salinity sources in freshwater aquifers. In practice however, alteration of these ratios by cation exchange and redox reactions make a simple application of this approach unreliable (Whittemore, 1983).

Cl is only rarely involved in sorption or ion-exchange reactions in ground-water systems and is involved in precipitation reactions only from solutions saturated with respect to halite and others halide salts (Feth, 1981). Accordingly, any change in the concentration of Cl in a ground-water mass at less than halite saturation which is not in contact with Cl salts can be assumed to be the result of mixing with other ground-water masses that contain differing concentrations of Cl. A chemical species which changes concentration only as a result of mixing is said to behave conservatively. Br is very similar in chemical behavior to Cl and so can also be expected to behave conservatively in ground-water systems provided that there is no interaction with evaporite minerals. It is possible

that some Br could enter ground water from the decay of organic matter (Means and Hubbard, 1987; Whittemore, 1988).

Because Br and Cl can be assumed to behave conservatively, their concentrations in a simple mixture of two reasonably homogenous end-member waters with unique compositions plot along a linear trend between the compositions of the end members. In addition, a unique Br/Cl ratio exists for any given relative amount of the end members present.

Br/Cl ratios have been used to identify sources of high-chloride ground water in fresh-water aquifers (Whittemore, 1983; Whittemore and others, 1985). Mixing curves constructed using Br/Cl ratios have also been successful in identifying oil-field brines that have entered a fresh-water aquifer through seepage from brine evaporation pits (Whittemore and others, 1985).

Sr does not necessarily behave conservatively in the natural environment. Dissolution or alteration of common silicate minerals such as feldspars can add Sr to ground water. Dissolution or precipitation of sulfate or carbonate minerals such as gypsum, anhydrite, celestite, or strontianite can add or subtract strontium from ground water. Because of their small relative differences in atomic mass, ^{87}Sr and ^{86}Sr are not preferentially incorporated into a precipitating mineral. Thus, precipitating minerals may remove strontium from ground water; however, the $^{87}Sr/^{86}Sr$ ratio in the solution from which the mineral precipitates

will not be changed. Only dissolution of minerals with $^{87}Sr/^{86}Sr$ ratios different from that of ground water will change the $^{87}Sr/^{86}Sr$ ratio in ground water. In a mixture of two reasonably homogenous end-members with differing concentrations of dissolved Sr, a plot of $^{87}Sr/^{86}Sr$ against 1/Sr will yield a linear relation (Faure, 1977, p. 98-101).

The $^{87}Sr/^{86}Sr$ ratio provides information on the isotopic composition of sources of dissolved Sr in subsurface waters. As such, the $^{87}Sr/^{86}Sr$ ratio can provide information on the sources of dissolved Sr and can also be used to document rock-water interactions involving Sr. Examples of the use of the $^{87}Sr/^{86}Sr$ ratio in the study of subsurface waters includes the Mediterranean Coastal Plain of Israel (Starinsky and others, 1983); formation waters of the Canadian Shield (McNutt and others, 1984); and oil-field waters in southeastern Ohio (Sunwall and Pushkar, 1979), southern Arkansas (Stueber and others, 1984), central Mississippi (Saunders and others, 1988), southern Louisiana (Posey and others, 1985), central Kansas (Chaudhuri and others, 1987), the northern Rocky Mountains (Burtner, 1987), and the Michigan Basin (McNutt and others, 1987).

Values of $\delta^{18}O$ and δD provide information on the isotopic composition of H_2O in subsurface waters. Because $\delta^{18}O$ and δD are characteristic of the solvent rather than solutes, the value provides information on the source and history of subsurface water. Specific information which can be gained from values of $\delta^{18}O$ and δD include any history of

evaporation and alteration by isotope exchange with surrounding rocks or organic matter which may have affected the composition of ground water. Specific examples of the use of $\delta^{18}O$ and δD values in the study of saline ground waters include, but are not limited to, Posey and others (1985), Kharaka and Carothers (1986), and McNutt and others (1987).

APPENDIX B

CALCULATION OF GROUND-WATER SALINITY, DENSITY AND VISCOSITY FROM SPONTANEOUS POTENTIAL LOGS

The spontaneous potential (SP) log is one of the oldest and simplest types of borehole measurement. The following discussion of the origin of the SP is based on Wylie (1949; 1951) and Schlumberger (1972, p. 7-12 and p. 77-80).

The SP is the difference in electrical potential between an electrode suspended in a borehole in contact with the drilling fluid and a reference electrode at the surface. The value of SP recorded as a function of depth in a borehole constitutes the SP log. The static SP (SSP) is defined as the measured SP of a permeable geologic unit, such as a sand, minus the measured SP of an adjoining shale. In practice the SSP is measured as the deflection of the SP curve in a permeable unit from a baseline determined by the SP response of an adjoining shale. The SSP is the quantity used in the estimation of ground-water salinity.

The SSP consists of electrochemical and electrokinetic potentials. The electrochemical potential is related to activity gradients of ionic solutes between ground water and drilling fluid. The electrokinetic potential, also know as the streaming potential, is caused by flow of water containing ionic solutes through the drilling fluid. In practice, the electrokinetic portion of the SSP is usually

small and typically taken to be negligible when calculating ground-water salinity.

The electrochemical portion of the SSP can be further separated into the liquid junction potential (E_j) and the membrane potential (E_m). E_j is associated with migration of ionic solutes between ground water and drilling fluid in an electrically-neutral medium such as is approximated by a clean sand. E_m is associated with migration of ionic solutes between ground water and drilling fluid through a shale acting as an ion-selective membrane.

To illustrate how SSP is developed by solute migration, assume that the saline ground water can be characterized as an aqueous NaCl solution. When a borehole containing fresh drilling fluid penetrates sediments containing more saline ground water ionic solutes migrate along the the concentration gradient toward the borehole. In an electrically-neutral medium, Cl^- has a greater mobility than Na^+. As a result, Cl^- migrates more rapidly along the concentration gradient. The localized separation of charge associated with the differing migration rates gives rise to E_j. In contrast to clean sands, clay minerals in shales have a negative surface charge. This surface charge inhibits the movement of Cl^- but not the movement of Na^+ through the shale. The localized separation of charge created by inhibition of the movement of Cl^- gives rise to E_m. Using the assumption that the activity of ionic solutes is equal in both the clean sand and the adjoining shale we can write

$$SSP = E_j - E_m = K \log a_{gw}/a_{df} \qquad \text{equation B.1}$$

where,

K = temperature-dependant constant,

a_{gw} = activity of ionic solute in ground water, and

a_{df} = activity of ionic solute in the drilling fluid.

Calculation of K requires knowledge of the geothermal gradient in the area of interest or some other means of calculating subsurface temperature.

Electrical resistivity is easily measured in the field and is inversely proportional to ionic solute activity in an aqueous NaCl solution down to a resistivity of approximately 0.1 Ω-m. At less than approximately 0.1 Ω-m, the relation between resistivity and activity is non-linear and must be expressed in terms of an empirical approximation.
A relation between resistivity and activity allows equation B.1 to be written as

$$SSP = K \log R_{df}/ R_{gw} \qquad \text{equation B.2.}$$

A number of corrections must be made to the terms in equation B.2 prior to calculating ground-water salinity. The SSP does not fully develop is sands which are less than approximately 9.1 m (30 ft) thick. A sand-thickness correction factor used in correction measured SSP in logs which penetrate the Wilcox aquifer in central Louisiana has been discussed by Funayama (1990, p. 32-46). The correction

factor used in this dissertation is that of Atlas Wireline Service (1985) as cited by Funayama (1990, p. 46). In addition, measured values of SSP are lowered in hydrocarbon-bearing intervals by the hydrocarbon suppression effect (Asquith and Gibson, 1982, p. 29).

The term R_{df} in equation B.2 refers to the resistivity of the water component of the drilling fluid. Field resistivities were commonly measured on the bulk drilling fluid (drilling mud) prior to the early 1960's. More recently, field resistivity measurements are available for the water component of the drilling fluid (drilling mud filtrate). Where no resistivity data are available on the water component of the drilling fluid it must be estimated from the resistivity of the bulk drilling fluid. Funayama (1990, p 50) gives a relation between the resistivities of bulk drilling fluid and drilling fluid filtrate based on data from 428 logs penetrating the Wilcox aquifer in central Louisiana. This relation will be used to estimate the resitivities of drilling fluid filtrate in cases where only bulk drilling fluid resistivities are available.

Ground water salinities of greater than approximately 10,000 mg/L (Keys, 1990, p. 54) can be estimated from SP logs after the required corrections are made to the measured SSP and drilling fluid resistivities. The required corrections are incorporated into the algorithm of Bateman (1985, p. 182) as modified by Funayama (1990, p. 38). The

modified algorithm of Funayama (1990) was used to calculate ground-water salinities from SP logs in this dissertation.

The density of an aqueous NaCl solution can be estimated providing values of in-situ temperature, pressure, and salinity are known. Phillips and others (1981) as cited by Funayama (1990, p. 55-56) establishes a relation between temperature, pressure, salinity and density for aqueous NaCl solutions. This relation is largely insensitive to pressures expected in this study. Accordingly, pressure will be set to 1 bar in density calculations.

Assigning calculated densities of aqueous NaCl solutions to brines and saline waters in the Wilcox aquifer assumes that the behavior of these brines and saline waters approximates the behavior of aqueous NaCl solutions. Because the brines and saline waters in the Wilcox aquifer are dominantly NaCl solutions this assumption is justified.

The viscosity of an aqueous NaCl solution can also be estimated providing values of temperature, pressure, and salinity are known. The effect of pressure on viscosity of an aqueous solution is minimal within the range of pressures expected in this study. Funayama (1990, p. 59-61) gives a polynomial expression for the viscosity of pure water as a function solely of temperature. This polynomial expression was derived based on data of Vargaftik (1975). Phillips and others (1981) gives an expression allowing calculation of the ratio of viscosity of aqueous NaCl solutions to the viscosity of pure water as functions of temperature and the

salinity of the aqueous NaCl solution. Combining these expressions allows calculation of the viscosity of aqueous NaCl solutions as functions of temperature and salinity. As with density calculations, the estimation of ground-water viscosity assumes behavior similar to that of aqueous NaCl solutions.

APPENDIX C

MINERAL-STABILITY CALCULATIONS

CALCULATION OF EQUILIBRIUM CONSTANTS

Values of the equilibrium constant (K) are typically taken to be functions of temperature only under pressures characteristic of non-hydrothermal conditions in the Earth's crust. The dependence of K on temperature is calculated from the expression

$$\ln K(T/T_r) = -\Delta H^{o}_{r}(T_r)\, R^{-1}(1/T - 1/T_r) - (RT)^{-1}\int_{T_r}^{T} \Delta C^{o}_{r}(T)\,dT + R^{-1}\int_{T_r}^{T} \Delta C^{o}_{r}(T)\,d\ln T$$

equation C.1

as modified from Helgeson (1969) where,

$K(T)$ = equilibrium constant at the temperature of reaction,

$K(T_r)$ = equilibrium constant at the reference temperature,

ΔH^{o}_{r} = enthalpy of reaction at the reference temperature,

T = temperature of reaction in degrees K,

T_r = reference temperature in degrees K (typically 298 K),

R= universal gas constant, and

$\Delta C^{o}_{r}(T)$ = standard heat capacity of the reaction as a function of temperature.

While analytical expressions for heat capacity as a function of temperature exist for many rock-forming minerals the same is not true for species in aqueous solution. In this case, the temperature dependence of K may be calculated from the expression

$$\ln K(T/T_r) = -\Delta H^o_r(T_r)\, R^{-1}(1/T - 1/T_r) - (RT)^{-1}\Delta C^o_r|^T_{T_r}(T-T_r) + R^{-1}\Delta C^o_r|^T_{T_r}\ln(T/T_r)$$

equation C.2

as modified from Helgeson (1969) where,

$\Delta C^o_r|^T_{T_r}$ = the average standard heat capacity of reaction from tabulations of heat capacities at specified temperatures.

Tabulations of heat capacity data for rock-forming minerals and species in aqueous solution include Kelley (1960), Helgeson (1969), Helgeson and others (1978), and Robie and others (1979).

If heat capacity data is unavailable the last two terms on the right-hand side of equation C.2 can be ignored. The resulting relationship correctly predicts the dependence of K on temperature only if ΔH^o_r is independent of temperature and $\Delta C^o_r=0$. This is typically not the case when dealing with reactions between solids phases and dissolved species. Even with these limitations, the dependence of K on temperature can be adequately estimated at temperatures near the

reference temperature. Values of K as a function of temperature may also be calculated from polynomial expressions fit to experimental solubility data.

CALCULATION OF CHEMICAL ACTIVITIES IN AQUEOUS SOLUTION

The relationship between the chemical activity of a dissolved species and it total concentration in solution is given by

$$a_i = \gamma_i m_i \qquad \text{equation C.3}$$

where,

a_i = chemical activity of the ith species,

γ_i = activity coefficient of the ith species, and

m_i = molality of the ith species.

Activities of dissolved species are calculated using one of two basic approaches (1) the ion association (IA) method or (2) the Pitzer method. Sets of mass balance and mass action equations are simultaneously solved for each desired species in solution in both methods. Iterative approximations of γ and concentration of each species are made by successive simultaneous solutions of these sets of equations until a satisfactorily stable solution is reached. The IA method typically uses some form of extended Debye-Huckel equation to calculate values of γ for each species as a function of temperature and ionic strength of the

solution. Use of a Debye-Huckel type equation can lessen the accuracy of the IA method in high ionic-strength waters. The Pitzer method is a modified ion association approach using equations developed by Pitzer (1973) and applied to calculations of geological interest by Harvie and Weare (1980) and Harvie and others (1984). The Pitzer equations incorporate specific species-species interaction parameters into the calculation of γ as a function of temperature and ionic strength of the solution. This allows for more accurate estimates of γ in high ionic-strength solutions where species-species interactions become more important. A detailed discussion of various strategies and numerical methods using IA and Pitzer methods to calculate mineral stabilities in natural waters is beyond the scope of this work. Detailed explanations of numerical and thermodynamic approaches are found in the documentation accompanying several widely-used computer programs that calculate mineral stabilities. Some of these programs include PHREEQE (Parkhurst and others, 1980), PHRQPITZ (Plummer and others, 1988), SOLMINEQ.88 (Kharaka and others, 1988), and EQ3/6 (Wolery and others, 1990). A recent addition to available programs in SUPCRIT92 (Johnson and others, 1992) which expands the range of temperatures and pressures at which stability calculations can be made to 1000^{o}C and 5000 bars.

SATURATION INDEX

The thermodynamically-favored direction of a dissolution-precipitation reaction can be expressed in terms of the saturation index (SI),

$$SI = \log (\Pi a_p^{vp} / \Pi_r^{vr}) / K \qquad \text{equation C.4}$$

where,

Πa_p^{vp} = the product of the activities of product species in solution and

Π_r^{vr} = the product of the activities of reactant species in solution. A value of SI less than 0 favors mineral dissolution, a value of greater than 0 favors mineral precipitation, and a value of 0 ± 0.2 is considered to represent equilibrium conditions between the mineral and aqueous phases.

APPENDIX D

DATA FROM SP LOGS USED IN CALCULATION OF GROUND-WATER SALINITY, DENSITY, AND VISCOSITY

Table D.1 Data from SP logs used in calculating groundwater salinity, density, and viscosity on cross-section A-A'.

State ID number: 42953 Well name: A.B. Learned 1 Latitude: 31° 39' 48" Longitude: 91° 44' 12"	Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
Top of Wilcox (m below MSL): 985	1014 - 1057	43	- 93	1.0	105	1.045	0.62
Top of Big Shale (m below MSL): 1373	1420 - 1431	11	- 97	1.0	107	1.040	0.55
Base of Big Shale (m below MSL): 1391	1670 - 1674	4	-103	4.5	109	1.038	0.51
Rm: 2.1 ohm-m @ 80° F	1754 - 1758	7	-105	6.0	111	1.038	0.50
Rmf: NR	1766 - 1812	46	-103	5.0	106	1.034	0.49

State ID number: 46552 Well name: Harmon 2 Latitude: 31° 41' 34" Longitude: 91° 44' 57"	Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
Sec T R: 10 8N 7E	996 - 1018	22	- 98	1.5	104	1.045	0.62
Top of Wilcox (m below MSL): 936	1088 - 1094	6	- 91	1.5	96	1.040	0.59
Top of Big Shale (m below MSL): - -	1228 - 1242	14	- 96	2.0	99	1.039	0.57
Base of Big Shale (m below MSL): - -	1380 - 1392	12	-101	2.0	104	1.040	0.55
Rm: 2.4 ohm-m @ 84° F	1425 - 1434	9	- 98	2.5	101	1.037	0.54
Rmf: NR	1716 - 1724	8	-111	2.5	114	1.040	0.51
	1728 - 1759	31	-113	2.0	116	1.041	0.51

(table con'd.)

State ID number: 58303
Well name: Mitchell 1
Latitude: 31° 38' 14"
Longitude: 91° 43' 09"
Sec T R: 26 8N 7E
Top of Wilcox (m below MSL): 1017
Top of Big Shale (m below MSL): 1378
Base of Big Shale (m below MSL): 1385
Rm: 2.16 ohm-m @ 90° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1059 - 1071	12	-104	1.3	114	1.050	0.63
1146 - 1152	6	-100	1.0	108	1.045	0.60
1256 - 1263	7	- 91	2.0	96	1.037	0.56
1365 - 1377	12	-101	1.5	106	1.041	0.55
1404 - 1413	9	-104	2.0	110	1.043	0.55
1496 - 1505	9	-110	2.0	118	1.046	0.55
1615 - 1636	15	-114	1.8	122	1.046	0.53
1776 - 1780	4	-113	2.0	119	1.042	0.51
1897 - 1901	4	-114	6.5	122	1.042	0.49
1958 - 1964	6	-108	8.5	112	1.035	0.47

State ID number: 71149
Well name: Warren and Fisher 1
Latitude: 31° 30' 42"
Longitude: 91° 44' 17"
Sec T R: 10 6N 7E
Top of Wilcox (m below MSL): 1159
Top of Big Shale (m below MSL): 1538
Base of Big Shale (m below MSL): 1556
Rm: 1.76 ohm-m @ 90° F
Rmf: 0.88 ohm-m @ 145° F

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1199 - 1215	16	-100	1.0	120	1.051	0.60
1274 - 1291	17	- 90	1.5	106	1.042	0.57
1636 - 1642	6	- 96	1.8	110	1.039	0.52

(table con'd.)

State ID number: 78710
Well name: Fisher Lumber Z1
Latitude: 31° 29' 11"
Longitude: 91° 44' 49"
Sec T R: 22 6N 7E
Top of Wilcox (m below MSL): 1159
Top of Big Shale (m below MSL): 1538
Base of Big Shale (m below MSL): 1556
Rm: 2.38 ohm-m @ 82° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1223 - 1246	23	-101	1.0	107	1.043	0.58
1328 - 1344	16	- 96	1.0	100	1.038	0.55
1645 - 1658	13	-101	1.5	104	1.035	0.51
1781 - 1793	12	-115	1.5	121	1.042	0.51
1862 - 1867	5	-101	1.0	102	1.031	0.48

State ID number: 91316
Well name: Calvert 1
Latitude: 31° 35' 51"
Longitude: 91° 44' 16"
Sec T R: 10 7N 7E
Top of Wilcox (m below MSL): 1062
Top of Big Shale (m below MSL): 1478
Base of Big Shale (m below MSL): 1491
Rm: 1.58 ohm-m @ 97° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1214 - 1220	6	- 94	0.5	110	1.045	0.59
1299 - 1306	7	- 78	1.0	96	1.036	0.55
1365 - 1371	6	- 92	1.0	106	1.041	0.55
1559 - 1566	7	-105	2.0	122	1.046	0.54

State ID number: 92560
Well name: Concordia Unit 7
Latitude: 31° 31' 59"
Longitude: 91° 44' 35"
Sec T R: 3 6N 7E
Top of Wilcox (m below MSL): 1132
Top of Big Shale (m below MSL): 1507
Base of Big Shale (m below MSL): 1519
Rm: 2.19 ohm-m @ 90° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1248 - 1278	30	-108	1.5	117	1.048	0.59
1338 - 1344	6	-100	1.0	106	1.041	0.56
1683 - 1702	19	-119	1.0	129	1.048	0.53

(table con'd.)

State ID number: 104103
Well name: Gillis Heirs 1
Latitude: 31° 40' 26"
Longitude: 91° 44' 16"
Sec T R: 15 8N 7E
Top of Wilcox (m below MSL): 967
Top of Big Shale (m below MSL): - -
Base of Big Shale (m below MSL): - -
Rm: 1.72 ohm-m @ 95° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1034 - 1050	16	- 88	2.0	100	1.043	0.61
1350 - 1361	11	-92	0.8	103	1.040	0.55

State ID number: 116170
Well name: Quinn 21
Latitude: 31° 21' 25"
Longitude: 91° 44' 41"
Sec T R: 34 5N 7E
Top of Wilcox (m below MSL): 1379
Top of Big Shale (m below MSL): 1764
Base of Big Shale (m below MSL): 1782
Rm: 1.68 ohm-m @ 88° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1488 - 1495	7	- 94	4.0	109	1.040	0.54
1674 - 1680	6	- 97	1.0	112	1.039	0.51
1720 - 1741	21	- 92	1.5	104	1.034	0.50

State ID number: 121439
Well name: Angelina Lumber E1
Latitude: 31° 23' 12"
Longitude: 91° 44' 46"
Sec T R: 27 5N 7E
Top of Wilcox (m below MSL): 1379
Top of Big Shale (m below MSL): 1764
Base of Big Shale (m below MSL): 1782
Rm: 2.60 ohm-m @ 72° F
Rmf: 2.36 ohm-m @ 74° F

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1551 - 1577	26	-102	3.5	100	1.035	0.51
1814 - 1827	13	-125	3.0	129	1.046	0.51
1955 - 1966	11	-116	3.5	114	1.036	0.48
2122 - 2126	4	-128	1.5	129	1.042	0.47

(table con'd.)

State ID number: 125169
Well name: B.E. Quinn 1
Latitude: 31° 24' 00"
Longitude: 91° 44' 25"
Sec T R: 22 5N 7E
Top of Wilcox (m below MSL): 1323
Top of Big Shale (m below MSL): 1718
Base of Big Shale (m below MSL): 1729
Rm: 2.25 ohm-m @ 89° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1438 - 1450	12	-102	1.0	106	1.040	0.54
1679 - 1684	5	-108	1.0	112	1.040	0.51
1759 - 1773	14	-102	1.5	103	1.033	0.50
1908 - 1919	11	-113	1.5	115	1.038	0.48

State ID number: 153543
Well name: Quinn 1
Latitude: 31° 24' 39"
Longitude: 91° 44' 48"
Sec T R: 15 5N 7E
Top of Wilcox (m below MSL): 1308
Top of Big Shale (m below MSL): 1688
Base of Big Shale (m below MSL): 1706
Rm: 2.7 ohm-m @ 62° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1352 - 1358	6	- 99	0.5	108	1.042	0.56
1422 - 1432	10	-101	0.8	110	1.042	0.55
1439 - 1446	7	- 92	1.5	98	1.036	0.53
1586 - 1590	4	- 84	1.8	93	1.031	0.50
1730 - 1734	4	-101	2.0	108	1.036	0.50
1775 - 1780	5	-110	2.0	119	1.041	0.51
1894 - 1903	9	-107	2.0	113	1.036	0.48

(table con'd.)

State ID number: 170434
Well name: Ames 1
Latitude: 31° 32' 11"
Longitude: 91° 45' 06"
Sec T R: 34 7N 7E
Top of Wilcox (m below MSL): 1122
Top of Big Shale (m below MSL): 1500
Base of Big Shale (m below MSL): 1508
Rm: 2.46 ohm-m @ 80° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1170 - 1179	9	-100	1.0	105	1.043	0.59
1258 - 1265	7	-100	1.0	105	1.042	0.57
1443 - 1477	34	-106	2.5	111	1.042	0.55
1717 - 1730	13	-109	4.0	112	1.039	0.51

State ID number: 180772
Well name: Mobil WBL 1
Latitude: 31° 35' 28"
Longitude: 91° 45' 04"
Sec T R: 15 7N 7E
Top of Wilcox (m below MSL): 1068
Top of Big Shale (m below MSL): 1481
Base of Big Shale (m below MSL): 1491
Rm: 2.51 ohm-m @ 80° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1189 - 1204	15	- 94	1.0	97	1.039	0.57
1401 - 1420	19	- 89	1.0	95	1.035	0.53
1495 - 1505	10	-113	0.8	120	1.046	0.55
1595 - 1606	11	-116	1.0	122	1.046	0.54
1648 - 1668	20	-116	1.5	122	1.045	0.53
1724 - 1740	16	-113	1.3	116	1.041	0.51

State ID number: 202194
Well name: Fisher 15-14 1
Latitude: 31° 29' 33"
Longitude: 91° 44' 53"
Sec T R: 15 6N 7E
Top of Wilcox (m below MSL): 1180
Top of Big Shale (m below MSL): 1554
Base of Big Shale (m below MSL): 1568
Rm: 2.4 ohm-m @ 66° F
Rmf: 2.1 ohm-m @ 67° F

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1211 - 1232	21	-107	2.8	119	1.050	0.60
1293 - 1301	8	- 90	3.0	97	1.037	0.55
1620 - 1624	4	-102	3.3	110	1.039	0.52
1769 - 1773	4	-115	2.0	124	1.045	0.52

(table con'd.)

State ID number: 208440
Well name: Angelina Plantation 1
Latitude: 31° 17' 31"
Longitude: 91° 44' 33"
Sec T R: 27 4N 7E
Top of Wilcox (m below MSL): 1480
Top of Big Shale (m below MSL): 1886
Base of Big Shale (m below MSL): 1902
Rm: 2.26 ohm-m @ 75° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1925 - 1932	7	-108	2.5	115	1.037	0.48
2143 - 2149	6	-113	1.5	120	1.037	0.48

Table D.2 Data from SP logs used in calculating groundwater salinity, density, and viscosity on cross-section B-B'.

State ID number: 44942
Well name: Fisher E-9
Latitude: 31° 40' 29"
Longitude: 91° 45' 14"
Sec T R: 16 8N 7E
Top of Wilcox (m below MSL): 956
Top of Big Shale (m below MSL): - -
Base of Big Shale (m below MSL): - -
Rm: 2.0 ohm-m @ 88° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1008 - 1030	22	- 91	0.8	101	1.043	0.62
1109 - 1117	8	- 89	1.0	99	1.041	0.59
1129 - 1136	7	- 92	0.8	102	1.042	0.59
1202 - 1207	5	- 88	1.0	96	1.038	0.57
1257 - 1262	5	- 99	1.0	110	1.045	0.58
1382 - 1405	23	-113	1.0	128	1.052	0.58
1452 - 1461	9	-110	0.8	123	1.049	0.56
1534 - 1541	7	-113	0.5	125	1.049	0.55

State ID number: 52716
Well name: Curtis Huff 1
Latitude: 31° 42' 12"
Longitude: 91° 28' 54"
Sec T R: 46 8N 10E
Top of Wilcox (m below MSL): 1024
Top of Big Shale (m below MSL): 1429
Base of Big Shale (m below MSL): 1446
Rm: 1.8 ohm-m @ 107° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1406 - 1410	4	-107	2.0	116	1.046	0.56
1566 - 1576	10	-115	1.5	125	1.048	0.55
1759 - 1763	4	-111	1.5	118	1.041	0.51

(table con'd.)

State ID number: 54008
Well name: Miller 2-1
Latitude: 31° 41' 43"
Longitude: 91° 29' 54"
Sec T R: 1 8N 9E
Top of Wilcox (m below MSL): 1023
Top of Big Shale (m below MSL): 1394
Base of Big Shale (m below MSL): 1406
Rm: 1.81 ohm-m @ 82° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1000 - 1070	70	-100	1.0	120	1.053	0.64
1095 - 1101	6	- 96	1.0	114	1.049	0.62
1174 - 1179	5	- 99	1.5	116	1.049	0.60
1579 - 1588	9	-107	2.0	125	1.048	0.54
1645 - 1652	7	-110	1.3	129	1.049	0.54

State ID number: 105144
Well name: Harmon 1
Latitude: 31° 44' 47"
Longitude: 91° 44' 44"
Sec T R: 10 8N 7E
Top of Wilcox (m below MSL): 940
Top of Big Shale (m below MSL): - -
Base of Big Shale (m below MSL): - -
Rm: 2.27 ohm-m @ 85° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
972 - 1023	51	- 98	4.0	108	1.047	0.63
1322 - 1345	23	-102	0.8	109	1.043	0.56
1426 - 1463	37	- 92	1.0	96	1.034	0.53

State ID number: 106493
Well name: Ballina Farms, Inc. 1
Latitude: 31° 40' 30"
Longitude: 91° 40' 36"
Sec T R: 17 8N 8E
Top of Wilcox (m below MSL): 1018
Top of Big Shale (m below MSL): - -
Base of Big Shale (m below MSL): - -
Rm: 1.97 ohm-m @ 86° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1049 - 1056	7	- 94	0.5	106	1.046	0.62
1445 - 1452	7	- 94	0.5	103	1.038	0.54
1655 - 1661	6	- 91	0.5	98	1.032	0.50

(table con'd.)

State ID number: 111802
Well name: Ballina Farms 1
Latitude: 31° 40' 40"
Longitude: 91° 41' 10"
Sec T R: 18 8N 8E
Top of Wilcox (m below MSL): 1015
Top of Big Shale (m below MSL): 1420
Base of Big Shale (m below MSL): 1437
Rm: 1.60 ohm-m @ 92° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1101 - 1106	5	- 89	1.0	107	1.045	0.61
1265 - 1272	7	- 88	1.0	103	1.041	0.57
1438 - 1443	5	- 91	1.0	107	1.040	0.54

State ID number: 120110
Well name: Panola 1
Latitude: 31° 40' 28"
Longitude: 91° 36' 02"
Sec T R: 13 8N 8E
Top of Wilcox (m below MSL): 1045
Top of Big Shale (m below MSL): - -
Base of Big Shale (m below MSL): - -
Rm: 2.21 ohm-m @ 82° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1096 - 1102	6	- 91	1.0	99	1.04	0.60
1370 - 1380	10	- 94	1.5	100	1.04	0.54
1571 - 1582	11	-108	1.0	116	1.04	0.53
1657 - 1665	8	-108	0.8	116	1.04	0.52

State ID number: 147226
Well name: Ferris 1
Latitude: 31° 40' 25"
Longitude: 91° 42' 06"
Sec T R: 13 8N 7E
Top of Wilcox (m below MSL): 1010
Top of Big Shale (m below MSL): 1414
Base of Big Shale (m below MSL): 1425
Rm: 2.38 ohm-m @ 82° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1040 - 1047	7	- 91	1.0	96	1.040	0.60
1439 - 1443	4	- 91	0.8	99	1.036	0.53
1523 - 1541	18	- 94	0.5	96	1.033	0.51

(table con'd.)

State ID number: 183285
Well name: Huff 1
Latitude: 31° 40' 20"
Longitude: 91° 25' 11"
Sec T R: 52 8N 10E
Top of Wilcox (m below MSL): 1047
Top of Big Shale (m below MSL): - -
Base of Big Shale (m below MSL): - -
Rm: 2.35 ohm-m @ 75° F
Rmf: NR

Sand Interval (m below MSL)	Sand Thickness (m)	SSP (mv)	Ri (Ohm-m)	Salinity (g/kg)	Density (g/cc)	Viscosity (cp)
1087 - 1092	5	- 94	2.0	103	1.044	0.60
1192 - 1199	7	- 86	1.5	98	1.039	0.58
1608 - 1617	9	-114	2.8	126	1.048	0.54
1731 - 1735	4	-106	2.0	113	1.040	0.51

APPENDIX E

CALCULATION OF FLOW VELOCITIES OF BRACKISH WATER IN THE ALLUVIAL AQUIFER OF EASTERN MOREHOUSE PARISH

GLOSSARY OF TERMS

ℓ_1 = location of point 1 on the ℓ axis.

ℓ_2 = location of point 2 on the ℓ axis.

x_1 = location of point 1 along the x axis.

x_2 = location of point 2 along the x axis.

P_1 = pressure at point 1 caused by the mass of overlying ground water.

P_2 = pressure at point 2 caused by the mass of overlying ground water.

z_1 = elevation of the base of the fluvial channel at point 1.

z_2 = elevation of the base of the fluvial channel at point 2.

h_{f1} = height of the column of fresh ground water at point 1.

h_{f2} = height of the column of fresh ground water at point 2.

h_{s1} = height of the column of brackish water at point 1.

h_{s2} = height of the column of brackish water at point 2.

ρ_f = density of fresh ground water.

ρ_s = density of brackish water.

η_f = viscosity of fresh water.

η_s = viscosity of brackish water.

v_ℓ = average brackish water flow velocity in the ℓ direction.

v_x = average brackish water flow velocity in the x direction.

H = total force per unit volume acting on ground water.

H_ℓ = force per unit volume acting on brackish water in the ℓ direction.

k = permeability tensor.

K = hydraulic conductivity tensor.

ϕ = fraction of pore space present in sediments.

R_p = resistivity of water-saturated sediments.

R_w = resistivity of water occupying the pore spaces in a water-saturated sediment.

f = formation factor.

g = acceleration due to gravity.

FLOW-RATE CALCULATIONS

Given the density and viscosity of water and the porosity and hydraulic conductivity of sediment the rate at which water travels through sediment can be estimated by summing the forces acting on water due to pressure and elevation gradients. A more accurate calculation of the velocities of solutes in ground water requires knowledge of the effects of chemical retardation and hydrodynamic

dispersion. The following discussion details the estimation of the velocity of brackish water movement to the southwest along the easternmost fluvial channel in eastern Morehouse Parish, Louisiana (fig. 4.3).

The force per unit volume acting on ground water at any point can be expressed as

$$H = -(\nabla P + \rho g \nabla z) \qquad \text{equation E.1.}$$

If the axis of the easternmost fluvial channel in Morehouse Parish is taken as the ℓ direction (fig. E.1), equation E.1 can be simplified to one dimension giving

$$H = -(\partial P/\partial \ell + \rho g \partial z/\partial \ell) \qquad \text{equation E.2.}$$

Hydrostatic pressure at any point along the ℓ axis equals the force applied per unit area by the mass of overlying ground water such that $P_{\ell=1} = g[\rho_f h_{f1} + \rho_s h_{s1}]$ and $P_{\ell=2} = g[\rho_f h_{f2} + \rho_s h_{s2}]$. Assuming that $h_{s1} = h_{s2}$ and that ρ_f and ρ_s remain constant we can write

$$\Delta P/\Delta \ell = g\rho_f(h_{f2} - h_{f1})/(\ell_2 - \ell_1) \qquad \text{equation E.3.}$$

From figure E.1 $h_{f2} = h_{f1} + z' - \Delta h$ and

$$\Delta P/\Delta \ell = g\rho_f(z' - \Delta h)/(\ell_2 - \ell_1) \qquad \text{equation E.4.}$$

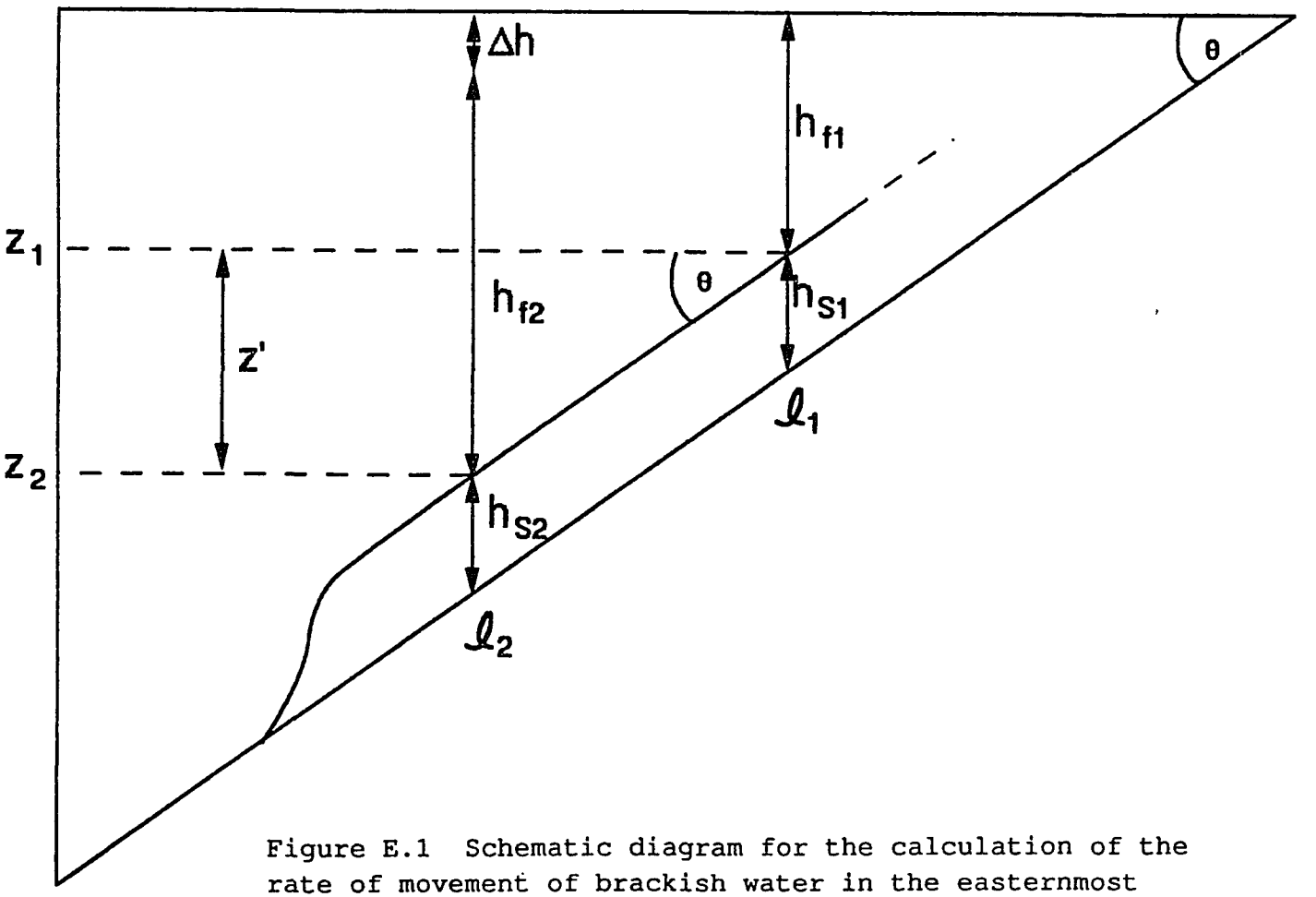

Figure E.1 Schematic diagram for the calculation of the rate of movement of brackish water in the easternmost fluvial channel.

From figure E.1 $z' = (\ell_2 - \ell_1) \sin \theta$ and $x_2 - x_1 = (\ell_2 - \ell_1) \cos \theta$. Using these trigonometric relationships and rewriting equation E.4 in terms of quantities measurable at the Earth's surface gives

$$\Delta P/\Delta \ell = g\rho_f[\sin \theta - \Delta h \cos \theta/ (x_2 - x_1)] \quad \text{equation E.5.}$$

Because we want to calculate the approximate velocity of brackish water in the ℓ direction, the second term on the right hand side of equation E.2 should be written as $\rho_s g(z_2 - z_1)/(\ell_2 - \ell_1)$. Again using the above trigonometric identities

$$H_\ell = -g[\rho_f(\sin \theta - \Delta h \cos \theta/(x_2 - x_1)) + \rho_s(z_2 - z_1) \cos \theta/(x_2 - x_1)] \quad \text{equation E.6.}$$

Assuming that the fluvial channel has a constant cross-sectional area, the average brackish water flow velocity is given by

$$v_\ell = kH_\ell/\eta_s\phi \quad \text{equation E.7.}$$

Figure 4.5 shows the trace of the induction resistivity log through test hole Mo-709. The average resistivity of the channel-fill is approximately 16 Ω m. A ground-water sample taken from well Mo-710 has a specific conductance of 2,670

μS/cm which is equivalent to a resistivity of approximately 3.7 Ω m. Using the above data

$$f = R_p/R_w = 16\ \Omega\ m/3.7\ \Omega\ m = 4.3 \qquad \text{equation E.8.}$$

The relation between f and ϕ for unconsolidated sands is given by

$$f = \phi^{-1.3} \text{ (Archie, 1942)} \qquad \text{equation E.9}$$

which yields ϕ = 0.32 for channel-fill sediments. The concentration of dissolved solids in ground water from well Mo-710 is approximately 1,800 mg/L. Thus, ρ_s is approximately equal to the density of an aqueous 2,000 mg/L NaCl solution at $20^{o}C$ (1.0014×10^{3} kg/m).

In order to calculate the average flow velocity of brackish water, point 1 was taken in the center of the mapped location of the fluvial channel at the Arkansas-Louisiana State line and point 2 was taken in the center of the mapped location of the fluvial channel at the approximate location of the freshwater saline water contact zone. The hydraulic conductivity of channel-fill type sediments in the study area was reported to be approximately 5,000 gallons ft^2/day (204 m/day) by Sanford (1973). Using the relation

$$k = K\eta_f/\rho_f g \qquad \text{equation E.10}$$

k was calculated to be approximately 2.4 X 10^{-10} m^2. From figure 4.3, the change in elevation of the base of the fluvial channel ($z_2 - z_1$) is approximately -15 m (-50 ft) and the horizontal distance ($x_2 - x_1$) is approximately 29.7 km (18.5 mi) giving a value of $\theta \simeq 0.03^{\circ}$. Sanford (1973) observed a drop of approximately 5 ft (1.5 m) (Δh) in water level at point 2 relative to point 1. Because the difference in η_f and η_s are small in this case equation E.7 can be written as

$$v_\ell = kH_\ell/\eta_f\phi \qquad \text{equation E.11.}$$

Values for g, η_f, and ρ_f are available in many compilations of standard reference data. The values used here are
$g = 9.81$ m/s^2,
$\eta_f = 10^{-3}$ kg/m s, and
$\rho_f = 10^3$ kg/m^3.
Evaluating equation E.11 gives v_ℓ = 9.3 m/yr (30 ft/yr). From figure E.1 $v_x = v_\ell \cos\theta$. Because $\cos\theta \simeq 1$ $v_x \simeq v_\ell$.

The methods used here to calculate the rate of southwesterly flow of brackish water provides an approximation only. The effects of dispersion and diffusion on the rate of advancement of the brackish water front have been ignored and simplifying assumptions have been made.

VITA

Glenn F. Huff was born in 1955 to Glenn T. and Regene P. Huff of Thomson, Georgia and graduated from Thomson High School in 1973. He received his B.S. in Geology from West Georgia College in 1980 and his M.S. in Geophysical Sciences from The Georgia Institute of Technology in 1984. Since completing his M.S degree, he has been employed as an environmental consultant, a high school teacher, a petroleum geologist, and a hydrologist. He began part-time work toward the Ph.D. in Geology at Louisiana State University in 1986 and appears, at long last, to be near completing the task.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Glenn F. Huff

Major Field: Geology

Title of Dissertation:

Hydrogeochemistry of Saline Waters in Aquifers of Tertiary and Younger Age in Northeastern Louisiana and Southeastern Arkansas

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Jeffrey G. Nunn

Lui-Heung Chan

Robert P. Romaire

Donald Dean Adrian

Date of Examination:

June 14, 1993